

1-7-75-1-13

N95- 23913

FOUR SPACE APPLICATION MATERIAL COATINGS ON THE
LONG-DURATION EXPOSURE FACILITY (LDEF)

John J. Scialdone and Carroll Clatterbuck
NASA Goddard Space Flight Center
Greenbelt, MD 20771
Phone: 301/286-6731; Fax: 301/286-2562

517-27

JIP

SUMMARY

Four material coatings of different thicknesses were flown on the LDEF to determine their ability to perform in the harsh space environment. The coatings, located in the ram direction of the spacecraft, were exposed for 10 months to the low-Earth orbit (LEO) environment experienced by the LDEF at an orbit of 260 nautical miles. They consisted of Indium Oxide (In_2O_3), Silicon Oxide (SiO_x), clear RTV silicone, and Silicone with Silicate-treated Zinc Oxide (ZnO). These coatings were flown to assess their behavior when exposed to atomic oxygen and to confirm their good radiative properties, stability, electrical conductivity, and resistance to UV exposure.

The flown samples were checked and compared with the reference unflown samples using high-magnification optical inspection, ESCA analysis, weight changes and dimensional changes. These comparisons indicated the following.

The 1000\AA SiO_x coating eroded uniformly, with minor changes in its radiative properties. The 100\AA In_2O_3 coating eroded completely down to the Kapton® backing, with resultant losses of reflectance. The RTV-615 showed erosion, with carbon (C) content losses, while the Si remained constant, with a doubling of the oxygen (O) concentration. The RTV-615 silicone with K_2SiO_3 -treated ZnO changed from flat to glossy white in appearance. It lost C, was etched, and increased its O content. The upper layers showed no remaining Zn or K. Losses of reflectance occurred within certain wavelength bands.

It was not possible to evaluate the experimental oxygen reaction rate using the calculated atomic oxygen fluence of 2.6×10^{20} atoms/cm² for the exposure of these coatings during the flight. The bakeout of the coatings was not carried out prior to the flight. Hence, the coating weight and dimensional losses included losses by outgassing products.

Kapton® is a registered trademark of the E.I. du Pont de Nemours Company

1. INTRODUCTION

Four coating samples prepared by the Materials Branch at GSFC were flown on the Long Duration Exposure Facility (LDEF) spacecraft, launched in 1984. The samples were mounted with many others in the Experiment Environmental Control Canister (EECC). The canister was identified as Experiment No. S0010, and was located in Tray B9, which was situated at an angle of 8.1° from the ram vector, as shown in Figure 1. The assembly of the test specimens in the flight canister and in the control canister was managed by NASA's Langley Research Center (LaRC).

The flight canister, shown in Figure 2, was provided with a drawer that opened and closed on command to expose the samples to the space environment while in flight. The container provided a clean, low-pressure inert gas environment while closed. A timer opened and exposed the samples 1 month after launch, and remained open for 10 months, at which time the drawer returned to the closed position to protect the samples during the remainder of the mission. The hermeticity of the drawer and canister was reconfirmed on the LDEF return, some 5 1/2 years after launch.

Table 1 shows the environmental exposure conditions as reported in Reference 1. The atomic oxygen fluence for the spacecraft (particularly for Row 9) and other data on the space environment are shown in Figures 3 and 4, taken from Reference 2 and 3.

For the 10-month exposure at an altitude of 260 nautical miles, the oxygen fluence is estimated to have been (from Figure 3 of the above reference) 2.6×10^{20} atoms/cm². The UV radiation exposure was 126,000 hours, as indicated in Table 1. The other environmental parameters are given in Table 1.

The four samples were located on the tray in the same row that included samples from the GSFC Optics Branch. Those samples consisted of various metallic coatings such as Au (gold), Pt (platinum), Os (osmium), Ir (iridium), and Al (aluminum) with MgF (magnesium fluoride) and SiO_x (silicon oxide).

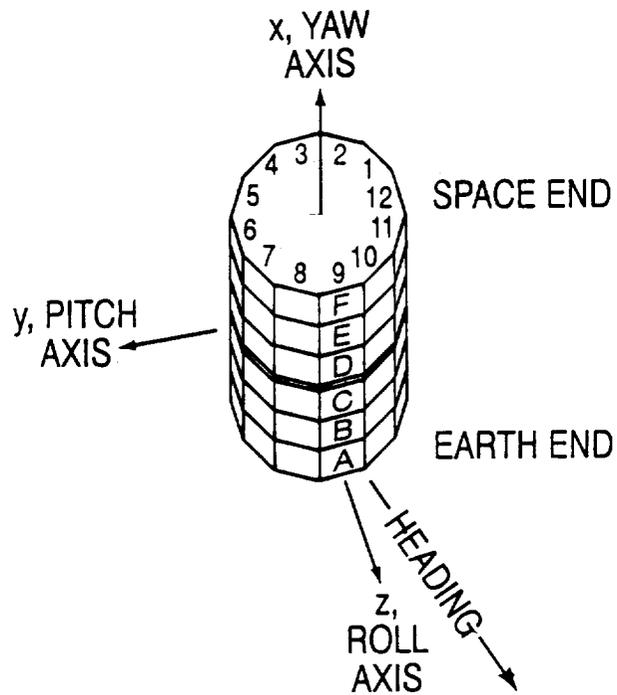


Figure 1. LDEF sketch and orbital configuration.

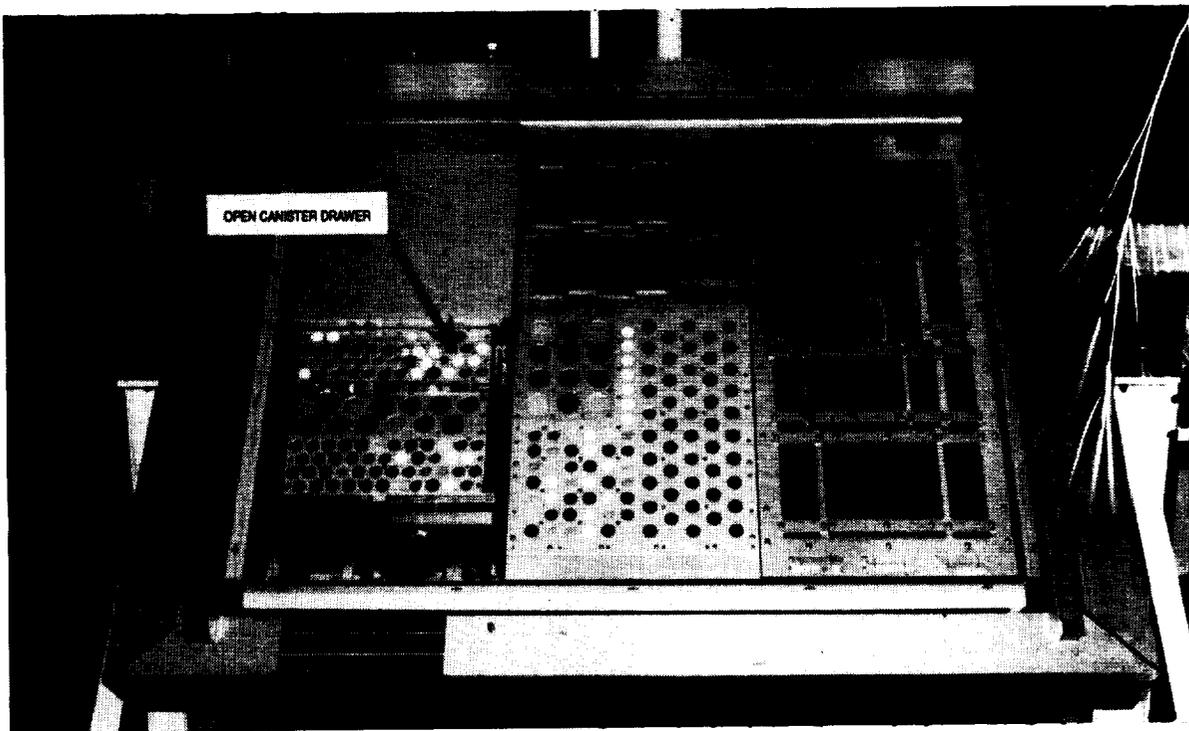


Figure 2. Photograph of Experiment Environmental Control Canister (EECC) with test specimen installed (Photo L-83-10,250).

Table 1. Preliminary Environmental Exposure Conditions

Atomic Oxygen* 0 to 10^{22} atoms/cm ² (wake to ram)	Vacuum 10^{-6} – 10^{-7} torr
UV radiation 100-400 nm; 16,000 hrs	Thermal cycles ~34,000 cycles: -20 to 190°F, ±20°
Particulate radiation e ⁻ and p ⁺ : 2.5×10^5 rad surface fluence Cosmic: <10 rads	Altitude 255–180 nautical miles
Micrometeoroid and debris 6000 particles from 0.1 mm to 2 mm	Orbital inclination 28.5°

*Updated value of 9.09E+21 as in Figure 4.

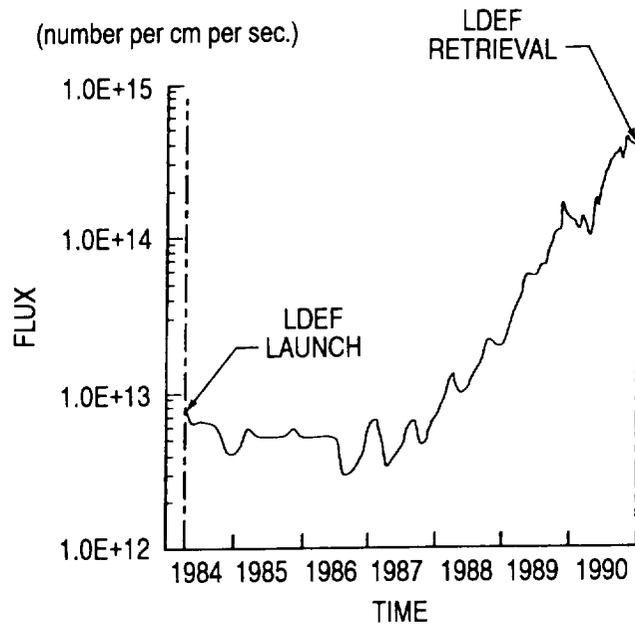


Figure 3. History of oxygen fluence on LDEF leading surfaces.

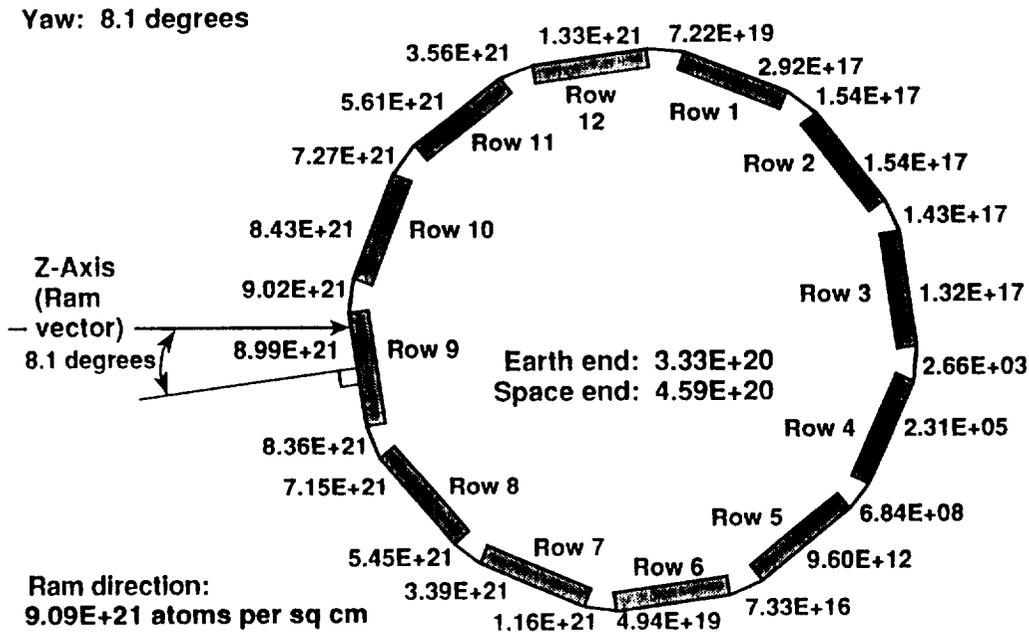


Figure 4. Calculated distribution of the total atomic oxygen fluence on each of the LDEF surfaces.

2. DESCRIPTION OF COATING SAMPLES

The four coating samples are shown schematically in Figure 5, indicating their compositions and the known dimensions. It is not known if, previous to the flight, those samples were baked out in vacuum to reduce their outgassing. We are assuming that they were not. The descriptions of the samples, the primary uses and advantages of the coatings, and available data on the samples follow.

Kapton®/VDA, 1000Å SiO_x (Sample #3)

This sample was composed of 1000 Å of SiO_x deposited on the vacuum-deposited aluminum (VDA) face of Kapton, which was attached to the aluminum support disk with 3M Corporation's Y-966 transfer adhesive. Data on the sample indicate that the weight of the assembled components was 4.345883 g and its total thickness was 0.1294 in. (0.3287 cm). The weight of the support disk was approximately 4.25987 g and its thickness was 0.1148 in. (0.2916 cm). No other data was given. The surface was described as "shiny metallized." This combination is often used as an environmental protective coating, is resistant to atomic oxygen exposure, and provides improved radiative properties after space environment exposure.

Kapton/VDA with 100 Å In₂O₃ (Sample #2)

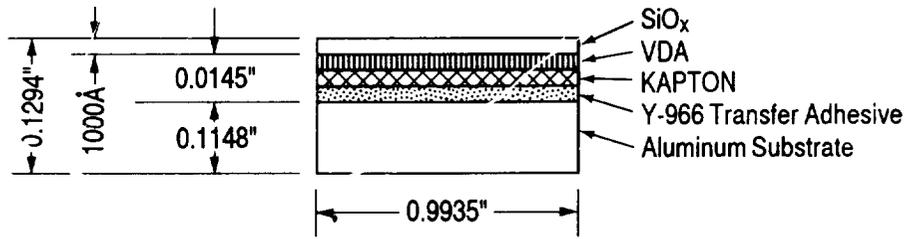
This sample consisted of 100 Å of indium oxide deposited on Kapton. The Kapton was attached with its vacuum-deposited Al face to the aluminum support disk with 3M's Y-966 adhesive. The data sheet indicates that the assembled sample weight was 4.328355 g and its thickness was 0.1271 in. (0.3228 cm). The support disk weight was approximately 4.259878 g and its thickness was 0.1160 in. (0.2946 cm). The surface was described as "yellow" and "shiny." The indium oxide coating provides sufficient electrical conductivity, has little effect on substrate solar absorption and emittance, and remains stable during long exposure in space to UV radiation and particle bombardment.

RTV-615 Silicone on Aluminum (Sample #2C)

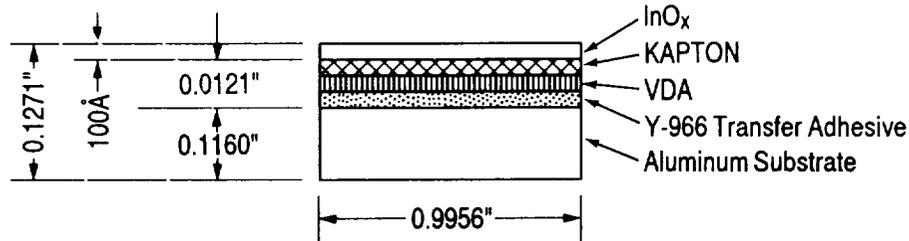
This sample consisted of devolatilized General Electric Corporation (GE) RTV-615 two-part silicone with an A/B parts-by-weight mix ratio of 10/1, which was bonded to the aluminum disk via GE primer SS4155. The data describe it as a clear silicone. The total thickness of the assembly was 0.1253 in. (0.3183 cm). The weight of the support disk was 4.25987 g and its thickness was 0.1127 in. (0.2862 cm). No other description was given. This combination is an environmental protective coating used as a sealant and is particularly resistant to atomic oxygen.

Kapton® is a registered trademark of the E.I. du Pont de Nemours Company

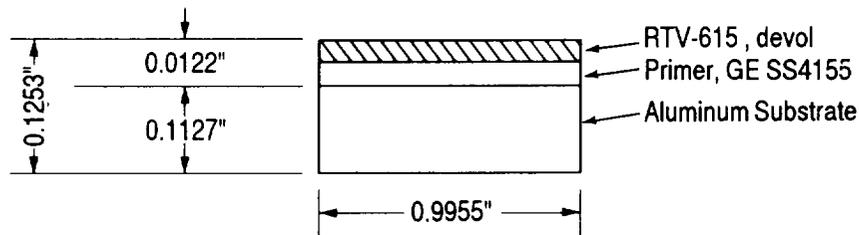
1. KAPTON®/VDA with 1000Å SiO_x coating



2. KAPTON®/VDA with 100Å In₂O₃ coating



3. RTV-615 Silicone on Aluminum



4. RTV-615 Silicone-Treated ZnO

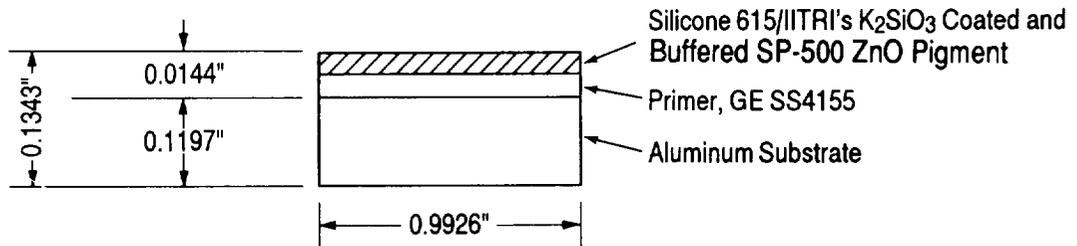


Figure 5. Side views of LDEF specimens (not drawn to scale).

RTV-615/Silicone-Treated ZnO (zinc oxide) (Sample #1A)

This sample consisted of GE's devolatilized RTV-615 two-part silicone with 68% of IITRI's K_2SiO_3 coated and buffered SP-500 ZnO pigment. The RTV-615 silicone had an A/B parts-by-weight mix ratio of 10:1. The material was bonded to the aluminum disk via GE primer, SS4155. The total weight was 4.55060 g and the total thickness was 0.1343 in. (0.3411 cm). The weight of the support disk was 4.25987 g and its thickness was 0.1197 in. (0.3040 cm). No other data were given. This combination is a thermal control coating and is used as a white paint for spacecraft and other structures. It is resistant to UV radiation exposure.

3. DATA AND MEASUREMENTS TAKEN

The effect of the space environment on these samples is indicated by providing the following descriptive parameters.

- The sample weight loss per unit area ($g\ cm^{-2}$)--This is the difference between the weight of the flight and control samples before and after the mission, ratioed to the exposed area of the flight samples.
- The sample thickness loss (cm)--This is obtained from the difference in thickness of the flight samples before and after the mission. Depending on the magnitude of the difference, one can determine the degree of coating loss attributable to the space environment.
- A percent thickness loss--This is based on the same assumptions used for the measurements of the coating thickness.
- A comparison of the spectral reflectance and the integrated absorption and emittance of the coatings before and after space environment exposure--The measurements were made using the P.E. λ -9 spectrophotometer.
- Surface analysis of the samples--The ESCA probe was used to provide elemental/chemical composition of the samples within a depth of 100 Å (up to some 50 monolayers) employing x rays to emit electrons.
- Photographic and microscopic documentation--This shows the reference and flight sample surface appearance and related evaluation of the changes that may have occurred following space exposure.

4. SAMPLE ANALYSES

1000 Å of SiO_x on VDA Kapton

Visual Inspection--The surface was highly reflective with some raised areas. The flight sample surface was slightly duller than the reference sample, with extremely fine discontinuities over the entire surface.

High-Magnification Inspection--The shape of the discontinuities was not discernible at 200 X magnification. There were no pinholes in the vacuum-deposited Al.

ESCA Analysis--The composition of both the flight and reference samples was similar, as shown by the spectrogram in Figure 6. The concentrations of Si and O remain constant through the thicknesses of both samples. Erosion may have been uniform over the surface. Peaks of silicone and oxygen are found within the various thicknesses.

Radiative Analysis--The reflectances vs. wavelengths are shown in Figure 7. The exposed sample shows an improved reflectance below 450 nm and above 700 nm. The integrated properties are $\alpha = 0.127$ and $\epsilon = 0.023$ for the flight sample, and $\alpha = 0.155$ and $\epsilon = 0.025$ for the reference sample.

Physical Analysis--The mass loss of the flight sample was 3.3×10^{-5} g or about 8.9×10^{-6} g cm⁻² of the exposed area. The thickness change amounted to 3.032×10^{-3} cm, corresponding to about 0.994% of the total sample thickness.

Oxygen Erosion--The change in thickness, 3.032×10^{-3} cm, is considerably more than the SiO₂ thickness of 1000 Å (1×10^{-5} cm). Some of the VDA Kapton was eroded. One cannot establish a reaction rate constant because the measured mass loss and thickness may include changes due to the sample's outgassing losses.

100Å In₂O₃ on VDA/Kapton

Visual Inspection--Figures 8 and 9 reveal uniformly oriented serrations in the highly reflective, gold-colored Kapton surface. Brushed marks on the aluminized surface are opaque with a golden hue and an aluminized color visible on only a few small areas.

High-Magnification Inspection--An etched, frosted appearance is visible at the brush marks under the undamaged areas.

ESCA Analysis--The flown coating sample (Figure 10) has a rough surface with visible erosion and delamination. The non-exposed surface appears shiny at the outer edge, with no visible damage. The exposed surface is severely eroded and gray in color, with scratch marks around the eroded area. The scratched and eroded areas are made up mostly of Kapton, with some traces of indium. The indium at those locations measured up to 0.95 atomic % while at the unexposed surfaces, the indium was 7 atomic %.

Mon Jun 22 13:58:34

M-Probe ESCA Console

User ID: LDEF

Filename	Spot	Res	Flood eV	Scans	Description
G080205.MRS	200x750 μ	3	1.0	1	LDEF.SiO _x +KAPTON,flight,60 sec sput
G080107.MRS	200x750 μ	3	1.0	1	LDEF.SiO _x +KAPTON,ref,60 sec sput

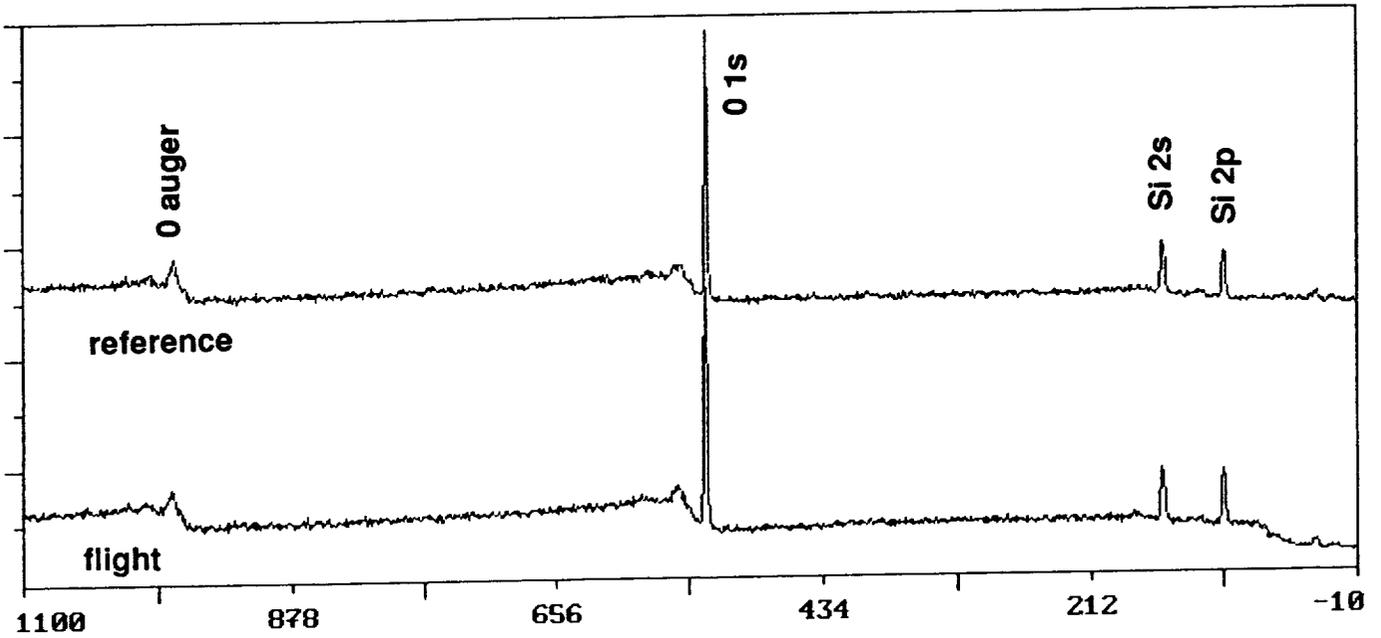


Figure 6. ESCA spectrum of 1000 Å of SiO_x on VDA/Kapton.

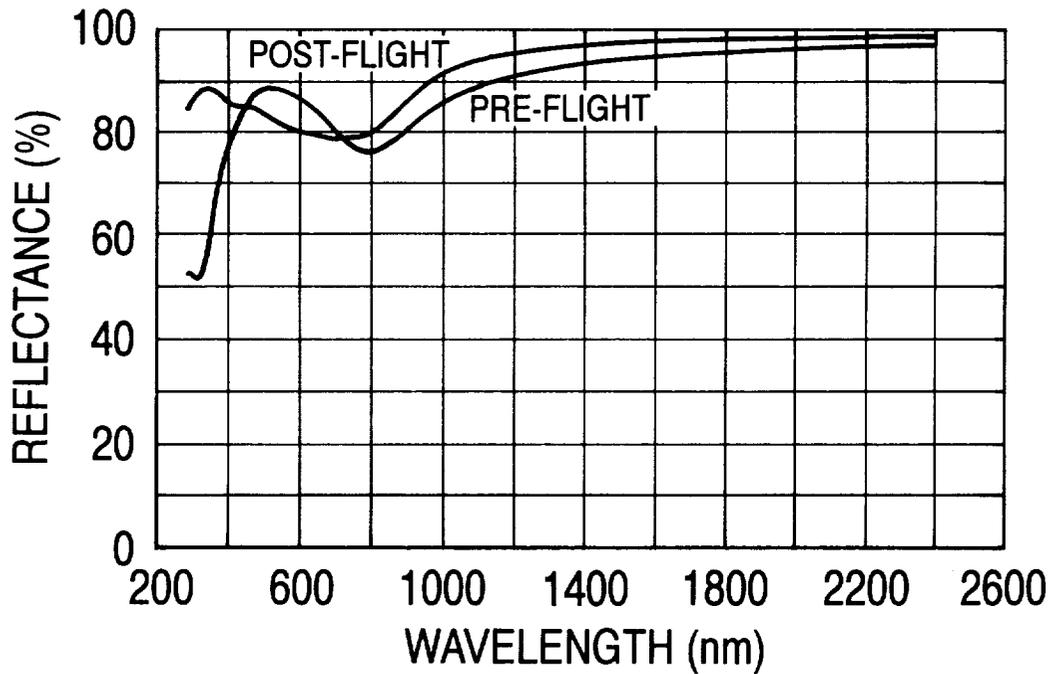


Figure 7. Reflectance of 1000 Å SiO_x coating on VDA/Kapton sample.

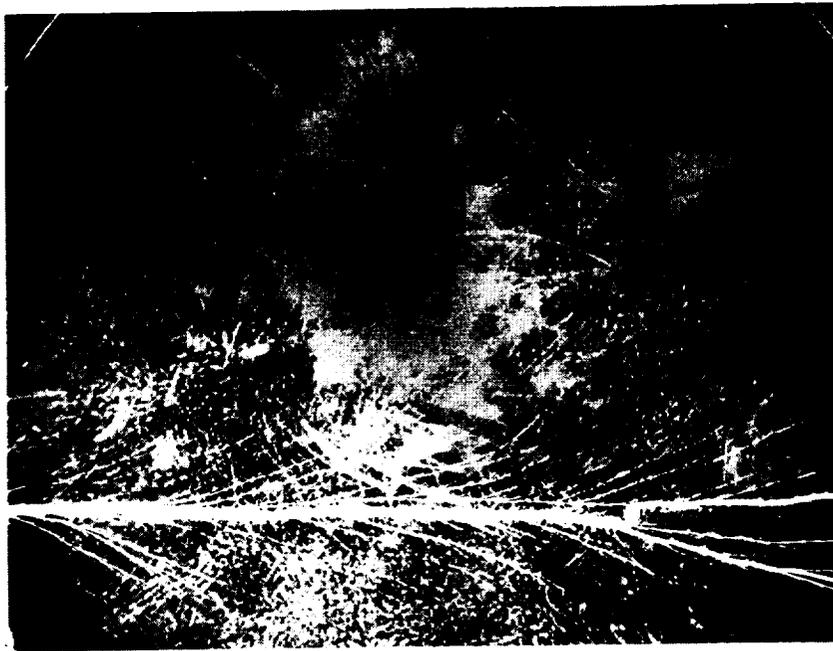


Figure 8. 100 Å In_2O_3 on VDA/Kapton (5.5X).

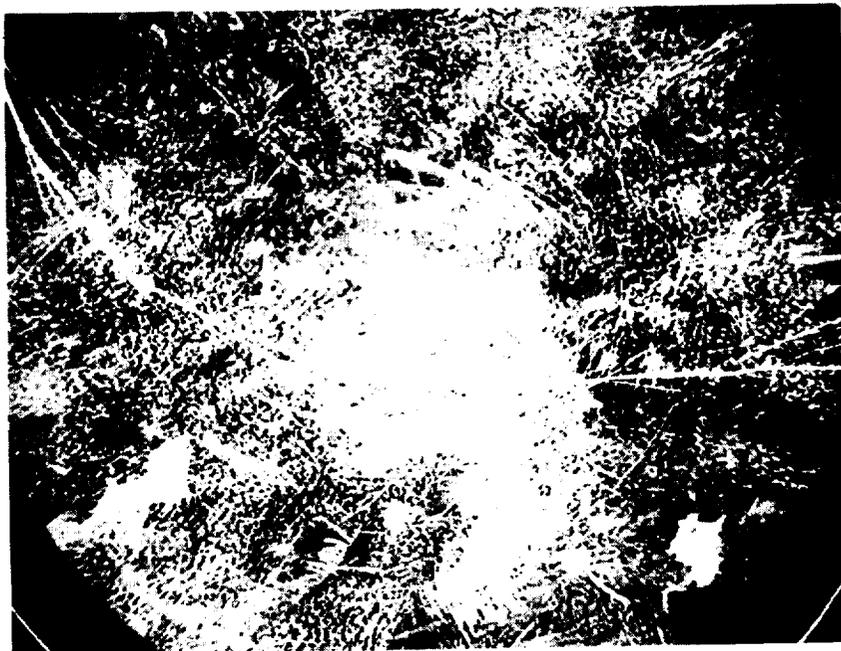


Figure 9. VDA/Kapton/ InO_x (5.5X).

Mon Jun 22 13:50:46

M-Probe ESCA Console

User ID: LDEF

Filename	Spot	Res	Flood eV	Scans	Description
G072910.MRS	200x750 μ	3	1.0	1	LDEF,VDA#2-KAPTON,center,60sec sput
G072903.MRS	200x750 μ	3	1.0	1	LDEF,VDA#2-KAPTON,reference, 60 sec

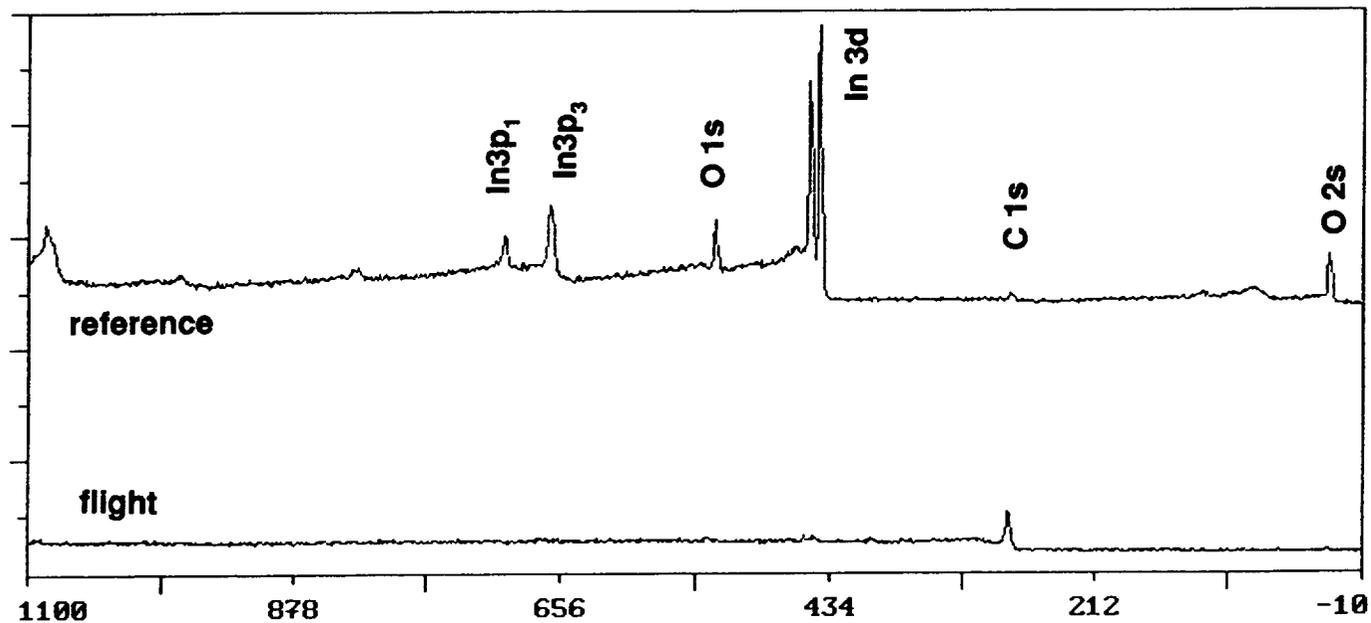


Figure 10. ESCA spectrum of sample with 100 Å of In₂O₃ on VDA/Kapton.

Radiative Analysis--Figure 11 shows the reflectances of the exposed and reference samples. About 10% reflectance loss occurred at wavelengths below 450 nm and about 5% loss occurred between 600 and 1600 nm. The integrated values are 0.391 absorption and 0.547 emittance for the flown sample and are 0.363 and 0.564, respectively, for the reference sample.

Physical Analysis--The mass loss for the sample was 0.001867 g, or about 5.37×10^{-4} g cm⁻² of exposed area. The thickness change amounted to about 5.08×10^{-3} cm, corresponding to about 1.538% of the total thickness.

Oxygen Erosion--The 100 Å (10^{-6} cm) of In₂O₃ and a considerable amount of the VDA/Kapton were eroded. In addition, considerable material and thickness must have been lost by outgassing in space. Not knowing if bakeout in vacuum was performed on the material before launch, it is not possible to estimate the reaction efficiency of the indium. However, the various analyses have indicated that the indium was completely eroded. The reaction rate for the Kapton is known to be about 3×10^{-24} cm³/atom from other orbital tests.

Devolatized RTV-615 Bonded on Al with SS 4155 Primer

Visual Inspection--The surface is clear and transparent with no noticeably changed features (Figures 12 and 13).

High-Magnification Inspection--Optical magnification shows banded networks with areas of contamination (possibly impacts) at focal points of several bands (Figures 12 and 13). The network of crack lines may have originated from solar exposure and from additional material losses causing thermal cracking.

ESCA Analysis--The erosion pattern is similar to that of the sample consisting of the same RTV with K₂SiO₃ and ZnO pigment. The flight sample shows carbon content of 1.5 atomic %, while the reference sample has 35 atomic %. The Si concentration did not change, while the O concentration doubled in the flight sample (Figure 14).

Radiative Analysis--The flight sample experienced a loss of about 5% in reflectance throughout the measured range of wavelength with respect to that of the reflectance sample. The integrated properties are $\alpha = 0.489$ and $\epsilon = 0.819$ for the flight sample, and $\alpha = 0.432$ and $\epsilon = 0.824$ for the reference sample (Figure 15).

Physical Analysis--The mass loss was 0.0037 g, or about 8.983×10^{-3} g cm⁻² of the exposed area. The thickness change amounted to about 8.63×10^{-3} cm, corresponding to about 2.617% of the total thickness.

Oxygen Erosion--The change in thickness, 0.0034 in. (8.63×10^{-3} cm), is considerably less than the thickness of the RTV and primer 0.0167 in. (4.24×10^{-2} cm). Under the assumptions that the loss was the result of the oxygen erosion, we could calculate the reaction efficiency.

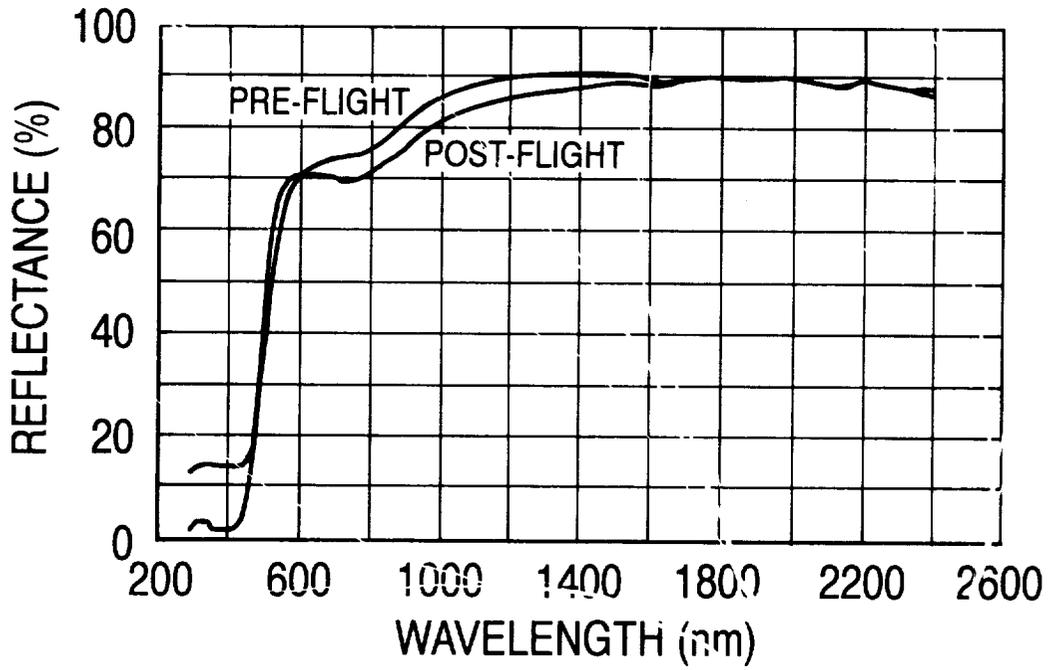


Figure 11. Reflectance of 100 Å InO₃ coating on VDA/Kapton sample.



Figure 12. Devolatilized RTV-615 bonded on Al with SS 4155 Primer (200X).



Figure 13. Devolatilized RTV-615 bonded on Al with SS 4155 Primer (25X).

Mon Jun 22 14:22:28 M-Probe ESCA Console User ID: LDEF

Filename	Spot	Res	Flood eV	Scans	Description
G09130S.MRS	400x1000μ	3	1.0	3	LDEF,RTU-clear,flight,60 sec sput
G09120S.MRS	400x1000μ	3	1.0	3	LDEF,RTU-clear,reference,1 min sput.

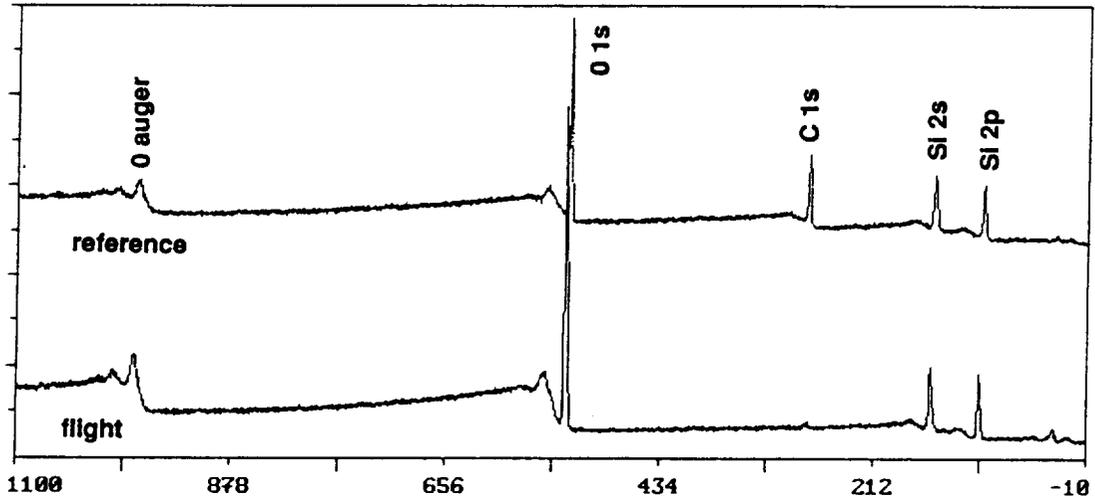


Figure 14. ESCA spectrum of sample with RTV-615 bonded on Al with SS 4155 primer.

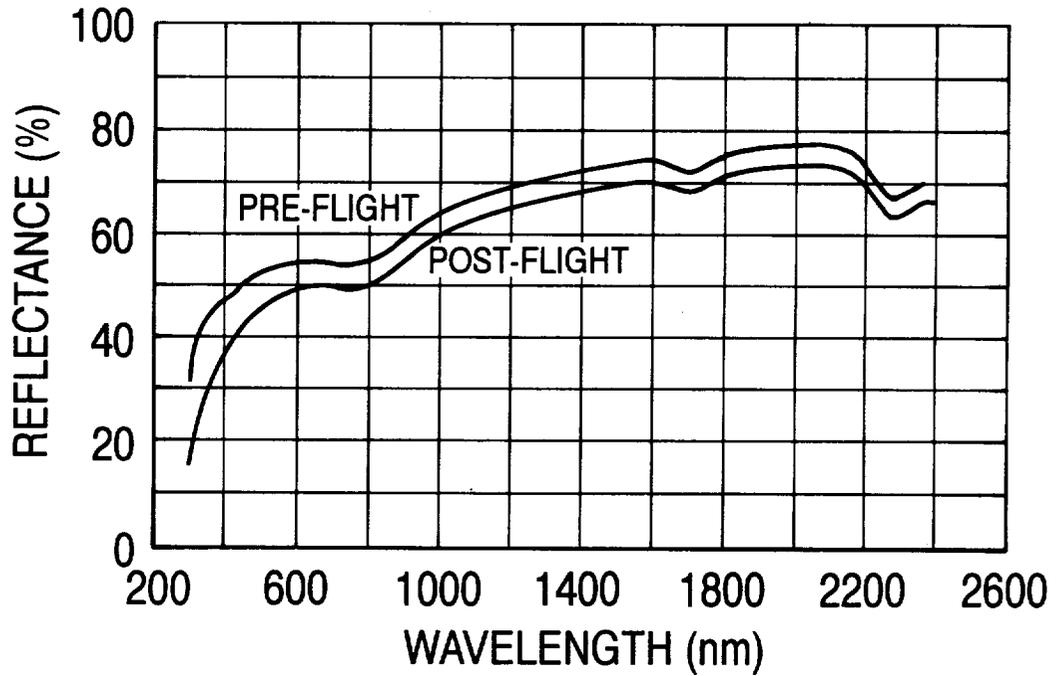


Figure 15. Reflectance of RTV-615 clear coating on aluminum.

However, calculations to estimate the reaction efficiency using the above data indicate a considerable oxygen erosion, much larger than the value of $6.25 \times 10^{-26} \text{ cm}^3/\text{atom}$ reported in reference 4. The discrepancy in order of magnitude must be assumed to have been produced by loss of material from outgassing.

RTV-615/Silicate-Treated ZnO

Visual Inspection--The flight sample surface appears slightly glossy and white, with raised agglomerated particles originating from the glossy matrix surface. The reference sample is flat white.

High-Magnification Inspection--The exposed flight sample surface is shown in Figures 16 and 17.

ESCA Analysis--This analysis (Figure 18) indicated considerable difference in the concentrations of carbon (C) between the flight and the reference specimens. The concentrations of Si between the two are about equal and constant through the thicknesses. The O and C concentrations differ. The C concentration decreases by 21 atomic % and O increases by 18 atomic % after 1 minute of etching. On the other hand, for the reference sample, the C decreases by 7 atomic % concentration and the O increases by 2 atomic % for the same etching time. No Zn or K peaks were found, even though the silicone was filled with potassium silicate and ZnO, indicating that they had eroded or that they had penetrated into deeper layers.

Radiative Analysis--The reflectance versus wavelength is shown in Figure 19. It shows some loss between 400 and 700 nm and between 1800 and 2100 nm. The integrated absorption is 0.201 and the emittance is 0.891 for the flown sample and 0.190 and 0.907, respectively, for the reference sample.

Physical Analysis--The mass loss was $8.27 \times 10^{-4} \text{ g}$, or about $2.33 \times 10^{-4} \text{ g cm}^{-2}$ of exposed surface. The thickness change amounted to $3 \times 10^{-3} \text{ in.}$ ($7.78 \times 10^{-3} \text{ cm}$), corresponding to about 2.142% of the total thickness.

Oxygen Erosion--Both the RTV and the silicate were eroded. The actual erosion and mass thickness are not known because of the possible loss by outgassing, and the calculation for the reaction efficiency could be erroneous. But, as indicated, the erosion did occur.

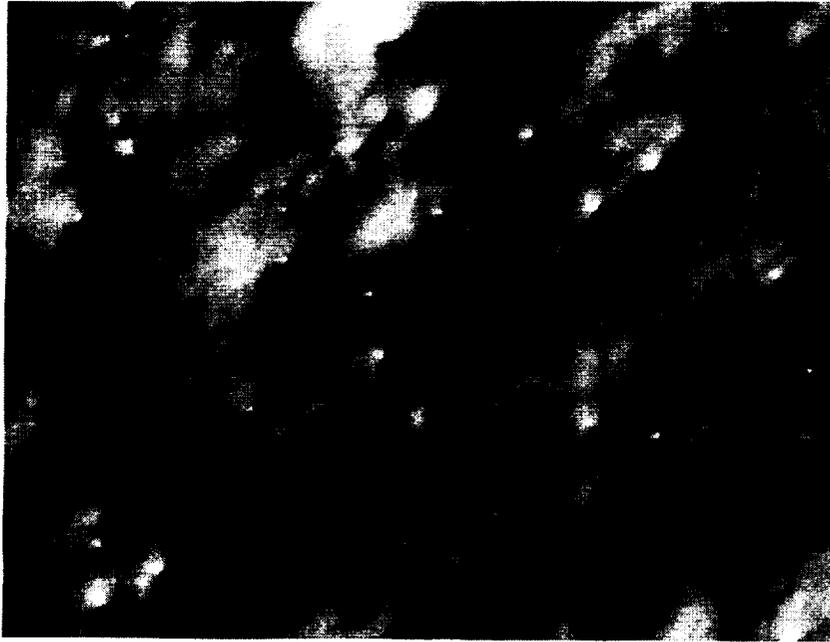


Figure 16. RTV-615/Silicone-Treated ZnO (38.5X).

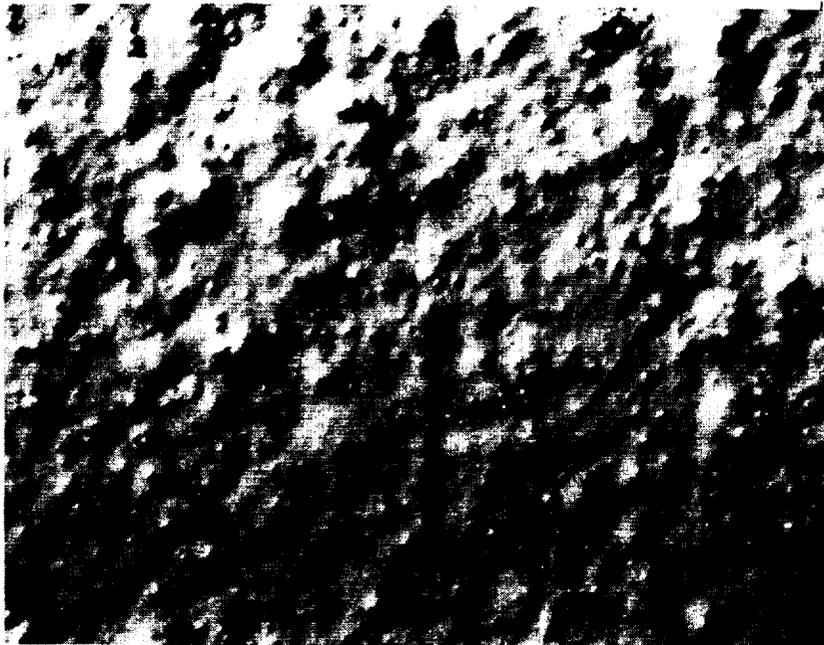


Figure 17. RTV-615/Silicone-Treated ZnO (16.5X).

Mon Jun 22 14:20:25 M-Probe ESCA Console User ID: LDEF

Filename	Spot	Res	Flood eU	Scans	Description
G091107.MRS	400x1000μ	3	1.0	3	LDEF.RTU-white.flight.3 min sput
G090807.MRS	400x1000μ	3	1.0	3	LDEF.RTU-white.ref.3 min sput.new lo

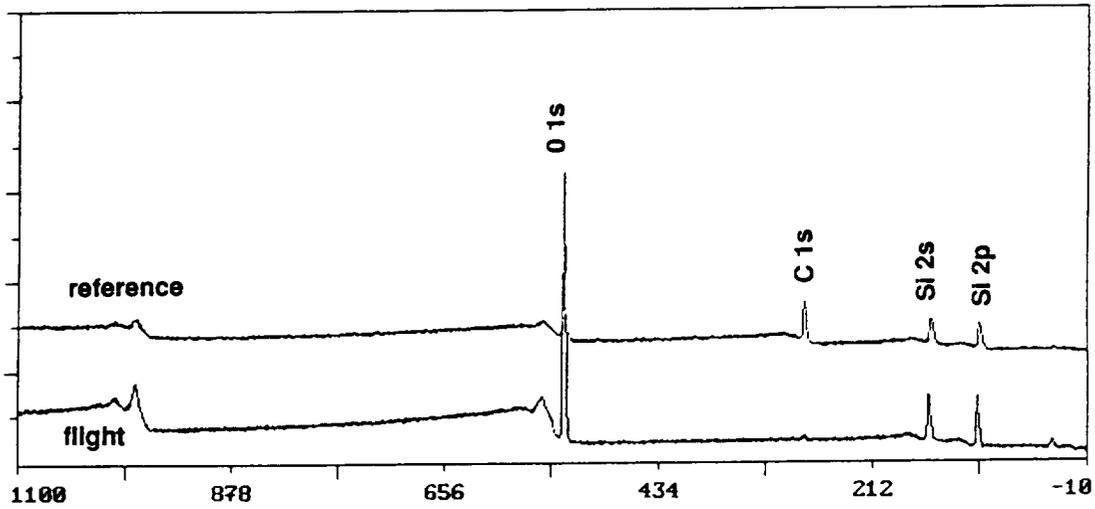


Figure 18. ESCA spectrum of sample with RTV-615 Silicone Treated with ZnO bonded on Al.

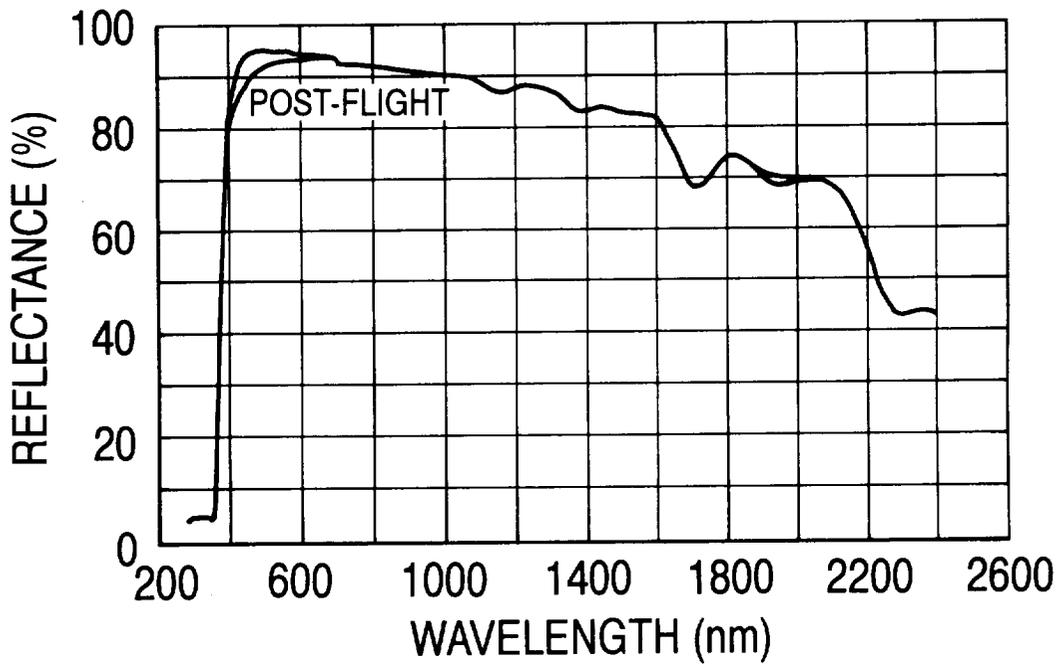


Figure 19. Reflectance of RTV-615/Silicone-Treated ZnO.

5. CONCLUSIONS

The four material coatings aboard the LDEF that were exposed directly to the space environment at an orbit of 260 nautical miles for 10 months, beginning 1 month after launch, have exhibited the following.

- **1000 Å of SiO_x on Kapton**--The sample of SiO_x was uniformly eroded. The concentrations of O and Si remained constant. Some improved reflectance occurred below 450 nm and above 700 nm.
- **100 Å In₂O₃ on VDA/Kapton**--The sample was severely eroded, with the indium reduced to less than 0.95 atomic % in comparison to the unexposed sample at 7 atomic %. The color changed from gold to gray. Kapton was exposed to the eroded areas and it exhibited substantial erosion. Losses of 5% to 10% in reflectance resulted below 450 nm and between 600 and 1600 nm.
- **RTV-615 Devolitized on Aluminum**--The sample surface shows erosion and banded networks originating from focal points. Carbon content dropped significantly. The Si concentration remained constant while the O concentration doubled with respect to the reference sample. Reflectance losses of about 5% occurred throughout the analyzed spectrum.
- **RTV-615 Silicate-Treated ZnO**--The flight sample surface changed from flat white to slightly glossy white. The C concentration decreased by about 21 atomic % while the O concentration increased by 18 atomic %, as the surface was etched. A comparable etching of the reference sample indicates a C drop of 7 atomic % and an O increase of 2 atomic %. No Zn and K were found, indicating either erosion or penetration deeper into the coating. Some loss of reflectance is noted at the wavelengths between 400 and 700 nm, and between 1800 and 2100 nm. The silicone was eroded.

An evaluation of the O reaction efficiency for the coatings exposed to a total O fluence of about 2.6×10^{20} atoms cm⁻² was not possible. The material losses and recessions must have included outgassing products, but these could not be determined. However, from the above analyses, general indications of these coatings' performance in orbit was possible.

6. ACKNOWLEDGMENTS

The authors are grateful to the following coworkers for their contributions to this work: Gloria Oh, for the ESCA analyses; Wanda Peters, for the reflectance measurements; and Diane Kolos, for the microscopic examination of the samples.

7. REFERENCES

1. Young, Philip R. and W. S. Slemm, *Analysis of the LDEF-Exposed Silvered FEP Teflon Thermal Blanket Material*, NASA TM 104096, December 1991.
2. Kinard, William H. and G. D. Martin, *Long Duration Exposure Facility Space Environment*, NASA CP 3134, p. 34, 1991.
3. Stein, Bland A., LDEF Materials Overview, *LDEF--69 Months in Space*, NASA CP 3194, pp. 741-789, April 1993.
4. Banks, B., et al., *Atomic Oxygen Effects on Materials*, NASA CP 3035, June 1988.



Organic Matrix Composite Protective Coatings for Space Applications*

Harry Dursch and Pete George
Boeing Defense and Space Group
P.O. Box 3999, M/S 82-32
Seattle, WA 98124
Phone: 206-773-0527, Fax: 206-773-4946

579-23
44432
18f

ABSTRACT

Successful use of composites in low Earth orbit (LEO) depends on their ability to survive long-term exposure to atomic oxygen (AO), ultraviolet radiation, charged particle radiation, thermal cycling, and micrometeoroid and space debris. The AO environment is especially severe for unprotected organic matrix composites surfaces in LEO. Ram facing unprotected graphite/epoxy flown on the 69-month Long Duration Exposure Facility (LDEF) mission lost up to one ply of thickness (5 mils) resulting in decreased mechanical properties. The expected AO fluence of the 30 year Space Station Alpha mission is approximately 20 times that seen on LDEF. This exposure would result in significant material loss of unprotected ram facing organic matrix composites. Several protective coatings for composites were flown on LDEF including anodized aluminum, vacuum deposited coatings, a variety of thermal control coatings, metalized Teflon, and leafing aluminum. Results from the testing and analysis of the coated and uncoated composite specimens flown on LDEF's leading and trailing edges provide the baseline for determining the effectiveness of protectively coated composites in LEO. In addition to LDEF results, results from Shuttle flight experiments and ground based testing will be discussed.

INTRODUCTION

As with all other spacecraft materials, successful use of composites in space depends on their ability to survive the various environments encountered during the spacecraft mission. Both AO and particulate radiation can cause a loss of mechanical properties. Thermal cycling induced microcracking results in dimensional stability and mechanical/thermal property changes. The very low vacuum levels of space cause moisture desorption resulting in dimensional changes and possible contamination of sensitive optics. High velocity impacts from meteoroid or space debris may result in cratering, penetration, or structural damage. Choosing the right coating can control or eliminate these environmental effects. The location on the spacecraft (internal vs external), orientation of the composite surface to the spacecraft's ram direction (orbital velocity vector), and the mission profile determine both the need for and the type of protective coating.

* Authorship of this paper was funded by NAS1-19427, Task 8. Testing of LDEF coated composites at Boeing Defense & Space was funded by Boeing IR&D.

PRECEDING PAGE BLANK NOT FILMED

The effects of the various space environments on unprotected organic matrix composites are summarized in the following paragraphs (references 1-4 contain papers discussing additional details).

- Atomic oxygen: AO induced erosion of bare composites is the most detrimental LEO environmental effect. Leading edge erosion has been well documented on the numerous bare composite specimens flown on LDEF's leading or near leading edges (total ram facing AO fluence was 9.09×10^{21} atoms/cm²). Typical depth of erosion loss of unprotected ram facing graphite epoxy (Gr/Ep) was approximately 0.005 inches or one ply of material. This loss resulted in reduced mechanical properties due to the reduced cross-section. AO did not cause any bulk changes in composites.

- Ultraviolet radiation: Minimal effect on composites. Limited to darkening of the surface resin layer

- Meteoroid and Debris: Composites retrieved from LDEF showed numerous impacts with the diameter and depth dependant upon the size and collision velocity of the impactor. Impact features on these composites generally took the form of broken fibers with missing matrix material. In some cases the diameter of the affected volume increased with depth (ref. 5)

- Particle Radiation: The threshold particle radiation dosage for organic matrix composite property degradation is approximately 10^8 to 10^9 rads, well above the total dosage seen by LDEF.

- Thermal Cycling: Thermistors on bare composite specimens flown on LDEF's indicated a maximum and minimum of approximately +180°F and -50°F over the first 4000 cycles of the 32,422 cycles seen by LDEF (ref. 6).

Figures 1 - 3 show three different Boeing built graphite fiber composite spacecraft structures, each possessing different protective coating requirements. Figure 1 is a photo of the Gr/Ep Hubble Space Telescope truss structure. This internal structure is shielded from any external environment with its temperature determined by the various layers of the spacecraft between it and the external spacecraft surfaces. This 252 lb structure highlights a property that composites provide, dimensional stability. The 16 ft focal length between the primary and secondary mirror supports is designed and manufactured to remain within 0.00005 of an inch during the temperature cycling associated with the LEO environment. Figure 2 shows a Gr/Ep antenna designed for use in a geosynchronous orbit (GEO) environment. The 6 ft diameter reflector has a base coating of vacuum deposited aluminum (VDA) overcoated with white inorganic coatings (YB-71 and Z-93). The VDA enhances the rf reflectivity and also serves as a good primer for the two inorganic coatings which provide passive thermal control. This coating scheme was subjected to twenty +250°F to -320°F thermal cycles and then exposed to high levels of particle radiation exposure. Test results met all program requirements. Although this coating scheme provides an excellent AO barrier, because of the GEO mission profile, AO protection was not a requirement. Figure 3 shows a prototype graphite/cyanate ester satellite bus structure designed for small launch vehicles such as Pegasus. This structure requires an exterior coating that 1) rejects heat generated by experiments mounted on decks within the structure and 2) provides protection for the thin exterior composite facesheet from AO induced erosion.

PROTECTIVE COATINGS

The use of a well designed and stable protective coating on externally mounted organic matrix composites both protects the underlying composite substrate from the exterior environment and alters the bare composite optical properties, resulting in reduced temperature extremes. Table 1 shows various protective coatings along with the range of optical properties possible with each coating.

Material	Solar Absorptance	Thermal Emittance
Bare Composite		
T300/934	0.90	0.73
Adhesively Bonded Aluminum Foil		
Bare aluminum foil	0.08 - 0.17	0.03
Chromic acid anodized - 1145 Al alloy	0.20 - 0.39	0.15 - 0.62
Chromic acid anodized - 6061 Al alloy	0.48 - 0.57	0.18 - 0.69
Sulfuric acid anodized - 5657 Al alloy	0.15 - 0.20	0.78 - 0.84
Vacuum Deposition		
Sputtered Al (420Å - 2520Å) smooth Gr/Ep surface	0.16	0.05 - 0.09
Sputtered Al (420Å - 2520Å) rough Gr/Ep surface	0.24	0.19 - 0.30
Vacuum deposited Al	0.22	0.04
Thermal Control Paints		
Z-93	0.14 - 0.17	0.92
YB-71	0.07 - 0.13	0.89 - 0.90
YB-71/Z-93	0.10	0.85
S13G/LO	0.15 - 0.19	0.88 - 0.91
A-276	0.21	0.87
Other Coatings		
Silverized Teflon (5 mil thick)	0.06	0.81
Silverized Teflon (2 mil thick)	0.07	0.66
Plasma sprayed aluminum	0.28	0.80

Table 1. Composite Protective Coatings

Ground based testing provides the initial screening for these coatings. Actual on-orbit exposure data is needed to verify ground based results and develop the necessary design confidence prior to these coatings being applied to spacecraft surfaces. Coatings flown on LDEF provide this data which has become the baseline for predicting coating performance in a LEO environment. It is interesting to note that LDEF was deployed prior to a thorough understanding of the effects of AO on organic composites. The coatings flown on LDEF composite specimens were selected as thermal control coatings. However, the majority of these coatings provided excellent AO protection. The following lists identify composite coatings that have been flown in space and undergone post-flight testing and analysis.

Protectively coated composites flown on LDEF:

- A-276 white titanium dioxide pigment in polyurethane binder with epoxy polyamide primer.
- BMS 10-60: white titanium dioxide pigment in polyurethane binder
- S13G: white zinc oxide in RTV 602 silicone binder (unknown if this was S13G/LO)
- White zinc oxide coating manufactured by General Dynamics
- Z-306: black carbon in polyurethane binder
- Tin/indium eutectic coating
- Leafing aluminum with epoxy binder with an epoxy polyamide binder
- Sputtered coatings: aluminum, aluminum/nickel, SiO₂/nickel, SiO₂/aluminum/nickel, SiO₂/chromium
- Aluminum thermal control tape

Composite coatings (without composite substrates) flown on LDEF:

- Chromic acid anodized aluminum
- Sulfuric acid anodized aluminum
- Z-93: white zinc oxide in a potassium silicate binder
- YB-71: white zinc orthotitanate (ZOT) in a potassium silicate binder
- YB-71 overcoated Z-93 combination
- Adhesively bonded silverized Teflon

Protectively coated composites flown on Shuttle experiments:

- Sputtered coated composites flown on STS-8, STS-41G, and STS-46 (EOIM-3)

TEST RESULTS

The following sections describe the results of ground based testing and testing of retrieved specimens for each category of protective coatings. Table 2 shows representative changes in optical properties of coatings flown on LDEF. The pre-flight values were taken prior to LDEF's deployment, the control values represent data taken on lab specimens after LDEF's retrieval, and the shielded specimens were either specimens facing LDEF's interior protected from the external environment or backsides of composite substrates on LDEF's exterior.

Specimen	Optical property	Preflight	Postflight (69 month exposure)			
			Control	Shielded	Leading	Trailing
Bare composite - graphite/epoxy	α	0.90		0.90	0.93	0.87
	ϵ	0.73		0.81	0.93	0.82
S13G-LO (ref. exp. S0069)	α	0.18			0.37	
	ϵ	0.90			0.89	
S13G/composite (McDonnell Douglas ctg)	α		0.14		0.19-0.21	0.34
	ϵ		0.90		0.88	0.89
Zinc Oxide (General Dynamics ctg)			0.48	0.46-0.59*	0.37	0.68
			0.89	0.88	0.92	0.88
A-276 (ref. exp. S0069)	α	0.25			0.24	
	ϵ	0.90			0.93	
TiO ₂ (A-276?)/composite (McDonnell Douglas ctg)	α			0.31	0.29	
	ϵ			0.90	0.94	
TiO ₂ (A-276?)/composite (General Dynamics ctg)			0.22	0.38-0.45*	0.35	0.59
			0.87	0.87	0.89	0.86
Leafing Aluminum/ composite	α		0.67	0.66	0.60	0.75
	ϵ		0.79	0.78	0.73	0.78
Z-93 (ref. exp. S0069)	α	0.14			0.15	
	ϵ	0.91			0.92	
YB-71 (ref. exp. S0069)	α	0.13			0.15	
	ϵ	0.90			0.89	
YB-71 over Z-93 (ref. exp. S0069)	α	0.10			0.11	
	ϵ	0.85			0.87	
CAA Al (tray clamps)	α	0.32	0.36	0.34	0.33	0.35
	ϵ	0.16	0.18	0.16	0.15	0.15
CAA Al (Exp S0010) - thick CAA	α	0.34			0.35	
	ϵ	0.75			0.75	
Silverized Teflon - 5 mil thick	α		0.07		0.07	0.08
	ϵ		0.81		0.78	0.81

* solar absorptance range due to varying amounts of contamination

Table 2. Optical Properties of Protective Coatings Flown on LDEF.

Anodized Aluminum Foil

Ground Based Testing

A series of NASA LaRC funded research tasks led to the selection of chromic acid anodized (CAA) aluminum foil as the optimum protective coating for Space Station's composite (now aluminum) truss structure. Reference 7 summarizes the findings of these studies into the development of sputter coatings applied directly to composite substrates and on adhesively bonded anodized aluminum foil. Other coatings evaluated included nickel-based coatings. Co-cured 0.002 inch thick CAA foil adhesively bonded to the 2 inch diameter composite tubes with a 0.003" thick layer of epoxy film adhesive was selected as the preferred coating for the following reasons:

- Environmental durability to the LEO environment including retention of foil to composite bond strength and retention of optical properties following 5000 hours of simulated UV exposure.
- Optical tailorability. As shown in Table 1, optical properties can be tailored to individual mission requirements by altering the anodizing parameters and/or aluminum alloy.
- Diameter of impact hole doesn't change with time limiting the amount of composite substrate subject to AO exposure following a meteoroid or space debris impact.
- Provides moisture/outgassing barrier.
- Anodizing and bonding process specifications developed.
- Excellent handling and abrasion resistance.
- Low cost and ease of manufacture.
- Excellent thermal conductivity minimizing temperature gradients due to shadowing of nearby structures.

Testing of Retrieved Hardware

No composites protectively coated with anodized aluminum foil have been flown on retrieved spacecraft hardware. However, CAA aluminum was used as part of LDEF's passive thermal management. The trays, tray clamps, space end thermal covers, and exposed surfaces of the primary structure were all CAA aluminum. This resulted in over 50% of the exposed surfaces on LDEF consisting of CAA aluminum. In addition, several LDEF experimenters flew CAA, sulfuric acid anodized, and dyed sulfuric acid anodized specimens that were anodized to a variety of thicknesses and optical properties. Results indicate that the CAA was very stable in its optical properties, but that contamination caused small increases in absorptance on surfaces exposed to low AO fluences. Sulfuric acid anodized surfaces appeared stable, although very little surface area was available for evaluation and no specimens were exposed to a high AO fluence environment. Only one type of dyed sulfuric acid anodize (Martin Black Anodize) was flown on LDEF. This specimen had increased infrared absorptance characteristics following its trailing edge exposure on LDEF² (ref. 8).

Vacuum Deposition

Testing of Retrieved Hardware

Composite substrates sputter coated with a variety of materials and thicknesses were flown on the leading edge experiment S0010, Exposure of Spacecraft Coatings. The combination of materials sputtered onto the Gr/Ep substrates were: aluminum, aluminum/nickel, SiO₂/nickel, SiO₂/aluminum/nickel, SiO₂/chromium, and aluminum/chromium. Figure 4 shows post-flight photos of two 1-in² Gr/Ep specimens flown on this experiment. The specimen on the left was uncoated while the specimen on the right was sputter coated with 600Å SiO₂ over 1000Å nickel. The outer-edge region of both specimens was protected by an aluminum holding fixture. The textured appearance is

the pattern of the breather cloth left in the resin rich surface during specimen fabrication. The 45-degree band pattern, for the uncoated specimen is most likely due to tow-to-tow material variations resulting in different erosion rates. The coated specimen exhibited no mass loss while the uncoated specimen lost 3-4 mils of material. Post-flight testing and analysis showed that while a total coating thickness of 400 Å retarded AO induced Gr/Ep erosion, total coating thicknesses as thin as 800 to 1000 Å eliminated any mass loss (ref. 9). Additional results also showed that rough surface morphology of composites can result in numerous protective coating defects of these ultra-thin coatings (ref. 10).

Space Shuttle flight STS-8, launched in September 1983, flew three sputtered coatings deposited on Gr/Ep substrates. Table 3 shows the various materials, thicknesses, and pre-flight and post-flight optical properties. Post-flight test results show the three coatings were generally unaffected by the 42 hour ram facing (3.5×10^{20} atoms/cm²) Shuttle exposure (ref. 11).

Specimens	Pre-flight α/ϵ	Post-flight α/ϵ
1600 Å of 0.999% pure nickel	0.52/0.45	0.52/0.45
600 Å SiO ₂ over 1600 Å nickel	0.50/0.27	0.49/0.27
800 Å Al ₂ O ₃ over 1800 Å aluminum	0.29/0.78	0.29/0.78

Table 3. Optical Properties of STS-8 Specimens

Thermal Control Paints with Composite Substrates

Testing of Retrieved Hardware

Over 55 organic matrix/graphite composite substrates overcoated with thermal control coatings were flown on LDEF. The specific coatings, A-276, BMS 10-60, S13G, Z306, leafing aluminum, zinc oxide mfg by General Dynamics, and an indium-tin eutectic were exposed to leading edge, trailing edge, and shielded environments on LDEF. Laboratory control specimens were also kept for the duration of LDEF's 69 month mission.

M0003-10 Results

LDEF Experiment M0003-10, Advanced Composites Experiment, included specimens supplied by McDonnell Douglas Space Systems Company (MDSSC) and General Dynamics Space Systems Division (GDSSD) to determine the effectiveness of protective coatings. MDSSC evaluated the TiO₂ (post-flight analysis shows this coating to most likely be A-276), S13G (unable to determine if this was S13G/LO), and leafing aluminum coated graphite/polyimide, Gr/Ep, and graphite/thermoplastic substrates. GDSSD evaluated TiO₂ (post-flight analysis and discussions with retired GDSSD personnel determined this coating was most likely A-276), ZnO (this was a proprietary coating developed by GDSSD somewhat similar to the S13G coatings), and an indium-tin eutectic coating (developed by GDSSD as a moisture barrier to prevent on-orbit composite dimensional changes associated with moisture desorption) protecting graphite-fiberglass fabric/polysulfone and graphite/epoxies. Most of the samples were composite strips 3.5 inches long x 0.5 inches wide with the coating applied to all six sides. Pre- and post-flight mass loss data was taken by The Aerospace Company (M0003 experiment integrator). Additional post-flight characterization occurred at Boeing Defense & Space including optical properties, cross-sectioning, and coating adhesion.

The optical properties for the TiO₂ coated specimens were typical of results found on A-276 coatings mounted throughout LDEF and provide an interesting study into the synergistic effects of the LEO environment. The leading edge AO fluences were high

enough to cause enough erosion of the polyurethane paint binder, removing the UV darkened binder seen on the trailing edge specimens. This AO induced erosion kept the UV damaged paint near original pre-flight absorptance levels. However, this erosion leaves the surface layers of the TiO₂ pigment in the A-276 without any binder. While the optical properties had not changed, the surface layers had lost their physical integrity and are easily damaged upon contact. The trailing edge specimens increased in solar absorptance due to the UV exposure darkening the polyurethane resin (no AO "cleansing" of the A-276). Tape peel testing on a leading edge specimen removed the pigment down to the stable binder. No material was removed during tape peel testing of shielded or control specimens. No erosion of the substrates was observed. Post-flight inspection showed that all the GDSSD woven graphite-fiberglass fabric/polysulfone (W-722/P-1700) specimens (coated, uncoated, lab control, and flight) had significant cracking. It is unknown if the cracking was present following cure or whether it slowly developed over time. The cracking was most likely due to coefficient of thermal expansion (CTE) mismatches between the fiberglass, graphite, and polysulfone matrix. On the coated specimens, these cracks extended up through the TiO₂ coating as shown in Figure 5. Photomicrographs taken at 400x appear to show minor AO induced erosion of the composite through the larger cracks on the leading edge.

Figure 6 shows leading edge and trailing edge MDSSC S13G coated composite specimens. The control and trailing edge optical properties were typical of LDEF data with the trailing edge specimen taking on a strongly discolored yellow appearance. The leading edge specimen took on a lightly discolored brown appearance but it experienced a much smaller increase in absorptance than other leading edge S13G/LO specimens. Unlike the A-276, tape peel tests showed no material removed from any of the specimens. Similar cracking was visible in the GDSSD ZnO coated W-722/P-1700 specimens as occurred in their TiO₂ coated specimens.

Figure 7 shows leading edge, trailing edge, and shielded leafing aluminum coated composite specimens. The leafing aluminum coating consists of aluminum flakes in an epoxy binder applied to a primed composite substrate. No other leafing aluminum specimens were flown on LDEF. Like the A-276 coated composites, the leafing aluminum specimens illustrate the synergistic effects of the LEO environment. The decrease in absorptance and increase in emittance for the leading edge specimen is attributed to removal of the epoxy binder exposing additional aluminum flakes. The increase in absorptance for the trailing edge specimen was caused by UV darkening on the epoxy binder. Tape peel testing removed some of the unsupported aluminum flakes on the leading edge specimen. No material was removed during tape peel testing of the control or trailing edge specimens. No erosion of the underlying composites was noted.

The indium-tin eutectic coating was developed as a composite moisture barrier. Minor visual differences between leading and trailing edge specimens with the exposed surfaces becoming dull and discolored compared to the control specimen. No erosion of the underlying composites was noted.

Pre- and post-flight mass loss data was taken by The Aerospace Company for all composite specimens flown on Experiment M0003-10 and all laboratory control specimens. These measurements were made after the samples had equilibrated in a constant temperature and humidity environment which eliminated moisture variations. The majority of the coated composite data is shown in Table 4. Analysis of this data illustrates the effectiveness of the coatings in protecting the underlying composite substrate from AO induced erosion. LDEF data showed that leading edge bare composites underwent a 2% to 4% mass loss. The coatings reduced this mass loss to negligible amounts similar to shielded or lab control specimens.

Specimen location	Uncoated - % mass change (# of specimens)	Coated - % mass change (# of specimens)
Leading edge - exposed	- 2.15 (1)	+ 0.02 (2)
Leading edge - shielded	- 0.41 (2)	- 0.07 (2)
Trailing edge - exposed	- 0.19 (1)	+ 0.73 (1)
Trailing edge - shielded	- 0.05 (2)	- 0.56 (1)
Lab control	- 0.17 (3)	- 0.05 (3)

Indium-Tin Eutectic Coating on GY70/X-30 Graphite/Epoxy flown by GDSSC.

Specimen location	Uncoated - % mass change (# of specimens)	Coated - % mass change (# of specimens)
S13G - Celion 6000/polyimide	-	+ 0.14 (1)
S13G - T300/5208	-	- 0.12 (1)
S13G - T300/P-1700	-	- 0.02 (1)
Leafing Al - T300/P-1700	-	- 0.41 (2)
TiO ₂ - T300/P-1700	-	- 0.18 (1)

Various coatings with various substrates flown by MDSSC. All specimens located on leading edge-exposed. No lab controls or uncoated specimens.

Specimen location	Uncoated - % mass change (# of specimens)	Coated - % mass change (# of specimens)
S13G - Trailing edge exposed	-	- 0.04 (2)
Leafing Al - Trailing edge exposed	-	- 0.11 (1)
- Trailing edge shielded	-	+ 0.05 (1)
TiO ₂	-	+ 0.01 (1)

T300 Graphite/Polyether Sulfone with various coatings flown by MDSSC. No lab controls or uncoated specimens.

Specimen location	Uncoated - % mass change (# of specimens)	ZnO Coated - % mass change (# of specimens)	TiO ₂ Coated - % mass change (# of specimens)
Leading edge - exposed	- 2.80 (2)	- 0.37 (6)	- 0.33 (6)
Leading edge - shielded	- 0.63 (2)	- 0.12 (6)	- 0.13 (6)
Trailing edge - exposed	- 0.08 (3)	- 0.04 (3)	- 0.03 (3)
Trailing edge - shielded	- 0.09 (3)	- 0.03 (3)	- 0.02 (3)
Lab control	- 0.07 (4)	- 0.01 (4)	- 0.03 (4)

Graphite-Fiberglass Fabric (W-722)/P-1700 with ZnO and TiO₂ coatings flown by GDSSD

Table 1. Mass changes for coated composite substrates flown on M0003-10 (data courtesy of The Aerospace Corporation).

M0003-8 Results

The electronics module cover for the leading edge experiment M0003-8 was an 11.75" x 16.75" Gr/Ep panel with thermal control coatings in three of the four quadrants. The following paragraphs summarize findings presented in reference 12. This panel was coated with two white urethane coatings, A-276 and BMS 10-60, and a black urethane coating, Z306. The fourth quadrant was left bare. One inch diameter mounting washers located at the corners and along each side shielded the underlying composite and coating. Temperature extremes were predicted, using pre- and post-flight optical properties, for each quadrant with the results showing maximum and minimum temperatures of 235°F to -70°F for the uncoated quadrant, 205°F to -70°F for the Z306 coated quadrant, and 60°F to -75°F for both the A-276 and BMS 10-60 quadrants. The bare composite lost an average of over 0.003 inches and the white coated quadrants showed no underlying composite erosion due to shielding by the AO stable TiO₂ pigment. The Z306 coating was severely eroded as both the carbon pigment and the polyurethane matrix were eroded by the AO. Some initial attack of the substrate under the Z306 coating was apparent. Extensive microcracking was observed in the black Z306 and bare quadrants. These cracks extended approximately one inch into the two white coated quadrants. The cracks, which appear to be related to thermal stresses, propagate up through the white coatings.

Figure 8 is a 3D plot of the data collected during a laser profilometry scan of a portion of the module cover. The approximately 1 inch square contains a circular region shielded from AO attack by one of the mounting washers. The A-276 coating covers the rear left half of the panel segment. This shows several interesting features including three distinct height levels, contaminant shielded area, and an impact site.

The five most prominent impact sites in this panel were cross-sectioned to investigate coating and substrate damage (figure 9 shows four of these five impacts). All five impacts happened to occur in the A-276 coated quadrant and were severe enough to have breached the coating, exposing the underlying composite. The deepest crater (upper right-hand corner) was over 0.015" deep (three plies). These impacts have many of the same features along with some distinct dissimilarities. Four of the five displayed an inverted hat shape (three very strongly) with the fifth impact site (lower right-hand corner), which does not have this shape, displays extensive crushing and displacement of material. No indications of A-276 coating undercutting by AO were visible in any of the five sites.

As shown in figure 9, pin-hole or impact damage through coatings will expose the underlying composite to AO attack. Reference 13 discusses an analytical approach used to determine reduction in properties of two-inch diameter Gr/Ep tubes from impact damage and subsequent AO induced erosion. Results show a hole diameter ≤ 0.2 " completely through a 0.06" thick tube causes a maximum reduction in the tube's EI (stiffness x inertia) of only 7%.

Space Shuttle flight STS-46, launched in July, 1992, flew an experiment titled Evaluation of Oxygen Interactions with Materials Experiment-3 (EOIM-3) for 42 hours of ram facing exposure (2.3×10^{20} atoms/cm²). Included in the 82 different materials flown on EOIM-3 were three ceramic coated graphite/thermoplastic (PEEK) composites coated with boron nitride/alumina ($\alpha = 0.39/\epsilon = 0.80$), alumina (0.35/0.82), or a plasma sprayed alumina. No measurable changes in optical properties and no visual or mass loss changes occurred for the coated PEEK substrates (ref. 14). AO erosion of the unprotected PEEK was ≈ 2 microns. Post-flight ESCA did show a differentiation of constituents may have occurred during the application of the boron nitride coating. In addition to these EOIM-3 results, two bare Gr/Ep specimens that were previously flown on LDEF were flown again on EOIM-3. One specimen was from the LDEF's trailing edge and the other had been shielded on LDEF, exposed only to vacuum. EOIM-3 post-flight testing showed the LDEF shielded specimen eroded much faster than the specimen that had been exposed on LDEF's

trailing edge. ESCA analysis revealed that silicone contamination existed on the trailing edge specimen which provided some protection against AO erosion (ref. 15).

Ground Based Testing

Reference 16 discusses the results of The Aerospace Corporation's study into the effects of thermal cycling of YB-71 coated Gr/Ep substrates. A second goal of the study was to evaluate the quality of different coating application processes. Five specimens of Gr/Ep coated with VDA were distributed to five participants interested in testing zinc orthotitanate (ZOT) application procedures and the ability of ZOT coatings to withstand thermal cycling from -275°F to +265°F. The participants were Boeing, Hughes Aircraft Company, TRW, JPL, and IITRI (manufacturer of YB-71). While results showed a variation in coating adhesion between the five sets of specimens, all the ZOT coatings performed adequately up to the maximum number of thermal cycles, 440.

Thermal Control Paints without Composite Substrates

Testing of Retrieved Hardware

The Z-93 and YB-71 coatings flown on LDEF were almost unchanged after the 69 month mission. The YB-71 overcoated Z-93 specimen also was impervious to the LEO environment (ref.17) LDEF results show that either coating is an excellent choice for long term LEO exposure. In fact, Z-93 has been selected as the radiator coating for the International Space Station Alpha.

Ground Based Testing

Thermal control coatings possessing a low solar absorptance and high thermal emittance are needed for the Space Station solar dynamic power module radiator surfaces. Eleven candidate materials including white thermal control coatings (Z-93, YB-71, and S13G/LO), silverized Teflon with oxide protective coatings, sulfuric acid anodized aluminum, and a plasma sprayed aluminum oxide coating, were evaluated. Results of extensive ground based testing showed the Z-93 and YB-71 to be the most durable and best performing coatings for this application since they maintained their optical properties and did not show cracking following AO exposure and thermal cycling (ref. 18).

Silverized Teflon

Testing of Retrieved Hardware

Silverized Teflon consists of a 2 mil or 5 mil thick first surface Teflon layer with a 1500Å layer of silver deposited onto the Teflon and a 100Å layer on inconel on the backside to protect the silver. Adhesively backed silverized Teflon is available from Sheldahl and has proven to be an excellent AO barrier. LDEF Experiment S0069 used pressure sensitive acrylic adhesive to adhere the 2 mil thick silverized Teflon to an aluminum facesheet. Post-flight observations showed a brownish discoloration of the silverized Teflon ranging from light to dark brown. The absorptance varied from 0.10 to 0.49 depending on the amount of discoloration. Post-flight testing and analysis showed that the technique used to apply the material to the aluminum covers excessively stressed the material resulting in cracking of the silver and inconel layers. This exposed the adhesive to UV (Teflon is transparent to UV) causing the discoloration. An improved application technique has been developed. Keeping the silverized Teflon flat during release paper removal and reducing squeegee pressure during application of the material to the substrate seems to have eliminated the damage to the silver and inconel (ref.19).

Post flight testing of LDEF ram facing 5 mil thick Teflon thermal blankets showed a Teflon thickness decrease of approximately 1 mil. Ram facing Ag/Teflon took on a milky

appearance and increased surface roughness resulting in decreased specularly. Minimal changes in solar absorptance or thermal emittance occurred for either leading or trailing edges specimens (ref. 20).

Silverized Teflon was also used on hardware retrieved from the Solar Maximum Measurement (SMM) experiment. This hardware was retrieved by the Space Shuttle STS-41C after 50 months in LEO (this Shuttle mission also deployed LDEF). SMM was launched in February 1980 in a 310 nm orbit. After 10 months attitude control malfunctions required that SMM be placed in a spin stabilized orbit until it was repaired 40 months later. By this time the orbit had decayed to 265 nm. Post-flight investigation of the silverized Teflon on the exterior surfaces of retrieved hardware showed changes similar to those found on similar material flown on LDEF. There was no change in absorptance or emittance but the outer surface of the Teflon had become rougher, described by SSM investigators as "bristle like" (ref.21).

SUMMARY

Adhesively bonded coatings - Ground based testing has shown adhesively bonded anodized aluminum foil co-cured or secondarily bonded to composites to be an excellent protective coating. On-orbit optical properties of chromic acid anodized aluminum have proven to be very stable and these properties can be easily tailored to a specific mission requirement by varying anodizing parameters and/or aluminum foil alloy. Aluminum foil also offers the best meteoroid and debris impact resistance of any of the coatings. If a breach of the coating does occur, the foil will limit the amount of AO reaching the underlying substrate. The limited information concerning sulfuric acid anodizing also shows this to be a stable coating but without the wide range of optical properties available in the chromic acid anodizing process. Anodized foil is best suited for tubular or flat structures as it can be difficult to apply to irregular shaped surfaces. In addition, the chromium anodizing facilities are slowly being phased out due to the health hazards associated with chromium.

Silverized Teflon is a widely used thermal control material possessing very low absorptance/emittance ratios. LDEF results showed that the application technique used for applying adhesively bonded silverized Teflon is critical in ensuring good on-orbit durability. Silverized Teflon has shown good long term on-orbit performances with the suitability of using this material to protectively coat composites dependant upon the charged particle or AO fluences seen during the mission (ref. 20).

Vacuum deposited coatings - LDEF results show that extremely thin sputtered coatings offer excellent atomic oxygen protection. Coatings as thin as 800Å eliminated any AO induced erosion of the composite substrate. Sputtering a layer of SiO₂ over the base metal layer provides the required emittance. For these coatings to be effective all composite surface irregularities must be adequately coated. The limitation to these coatings is the complexity associated with the need for vacuum during the coating process.

Thermal control coatings - Most space qualified thermal control coatings will provide the needed environmental protection and optical property retention for short term missions. The organic based coatings, such as S13G/LO and A-276, offer a good coefficient of thermal expansion (CTE) match with composite substrates and good coating/composite adhesion strength. For longer term missions two ITRI coatings, YB-71 and Z-93, provide the necessary protection and retention of optical properties. While no Z-93 or YB-71 coated composites have been retrieved from space for post-flight testing, LDEF data has shown excellent optical property retention and good bond strength retention to aluminum substrates. Successful application of these brittle ceramic coatings to an organic composite

substrate is rather complex, requiring careful application on a contaminate free surface. The application process used on the antennas shown in figure 2 consisted of a layer of VDA applied to the composite surface followed by a layer of hand rubbed Z-93 and then a spray application of YB-71. Boeing is currently developing a ZOT application specification eliminating the need for VDA and hand-rub application of the Z-93. Future flight experiments will be needed to verify this approach.

ACKNOWLEDGEMENTS

Richard Mell, AZ Technologies for providing assistance in verifying the type of the coatings flown on M0003-10. The Aerospace Corporation's Corporate Archives for providing timely assistance in acquiring photos and post-flight observation information on the various coated composites flown on M0003-10.

REFERENCES

- 1) Levine, A.S.: "LDEF 69 Months in Space, First LDEF Post-Retrieval Conference", NASA CP-3134, February 1992.
- 2) Stein, B. A, Young, P.R.: "LDEF Materials Workshop '91", NASA CP-3162, November 1991.
- 3) Levine, A.S.: "LDEF 69 Months in Space, 2nd LDEF Post Retrieval Symposium", NASA CP-3194, June 1992.
- 4) Whitaker, A.F, and Gregory, J.: "LDEF Materials Results for Spacecraft Application Proceedings", NASA CP 3257, October 1992.
- 5) See, T., et al: "Meteoroid and Debris Impact Features Documented on the LDEF: A Preliminary Report.", August 1990, NASA JSC Report # 24608.
- 6) Steckel, G.L, and Le, T.D.: "M0003-10 Advanced Composites Experiment", LDEF 69 Months in Space, First LDEF Post-Retrieval Conference, NASA CP-3134, February 1992, Volume 2, page 1041.
- 7) Teichman, L.A, Slemple, W.S., and Witte, W.G.: "Evaluation of Selected Thermal Control Coatings for Long-Life Space Structures", NASA TM 4319, January 1992.
- 8) Golden, J.L.: "Anodized Aluminum on LDEF", LDEF Materials Results for Spacecraft Application Proceedings, NASA CP 3257, October 1992, page 61.
- 9) Slemple, W.S, Young, P.R., and Witte, G.: "Effects of LDEF Flight Exposure on Selected Polymer Matrix Resin Composite Materials", LDEF 69 Months in Space, First LDEF Post-Retrieval Conference, NASA CP-3134, February 1992, Volume 2, page 1149.
- 10) Banks, B.: "Issues/Considerations and Performance Prediction of LEO Protective Coatings", Protection of Materials and Surface Finishes from the Low Earth Orbit Space Environment, Canadian Space Agency Forum, February 1992.

- 11) Visentine, J.T.: "Atomic Oxygen Effects Measurements for Shuttle Missions STS-8 and 41-G", NASA Technical Memorandum 100459 - Volume 1, September 1988.
- 12) George, P.E., Dursch, H.W., and Hill, S.G.: "Space Environmental Effects on LDEF Composites: A Leading Edge Coated Graphite/Epoxy Panel", 2nd LDEF Post Retrieval Symposium, NASA CP-3194, June 1992, Volume 3, page 923.
- 13) Bowles, D.E., Tenney, D.R.: "Composite Tubes for the Space Station Structure", 18th International SAMPE Technical Conference, October 1986.
- 14) Chung, S.Y. et al: "Flight- and Ground-Test Correlation Study of BMDO SDS Materials: Phase 1 Report", JPL Publication 93-31, December 1993.
- 15) Golden, J.L., et al: "Analysis of Selected Specimens from the STS-46 EOIM-3 Experiment" 3rd LDEF Post-Retrieval Symposium, NASA CP-3275, 1995.
- 16) Binegar, G.A. and Welch, J.W.: "Thermal Cycling Performance of YB-71 Zinc Orthotitanate (ZOT) Coatings Applied to Graphite/Epoxy Panels", The Aerospace Corporation Report No. TOR-0090(5404-21)-1, September 1990.
- 17) Wilkes, D.R, Brown, M.J., and Hummer, L.L: "Initial Materials Evaluation of the Thermal Control Surfaces Experiment (S0069)", LDEF 69 Months in Space, First LDEF Post-Retrieval Conference, NASA CP-3134, February 1992, Volume 2, page 899.
- 18) Dever, J.A., et al: "Evaluation of Thermal Control Coatings for use on Solar Dynamic Radiators in Low Earth Orbit", NASA TM-104335, June 1991.
- 19) Zwiener, James, et al: "Unusual Materials Effects Observed on the Thermal Control Surfaces Experiment (S0069)", LDEF 69 Months in Space, First LDEF Post-Retrieval Conference, NASA CP-3134, February 1992, Volume 2, page 919.
- 20) Pippin, H.G., Stuckey, W.S., Hemminger, C.; "Performance of Silvered Teflon Control Blankets on Spacecraft", LDEF Materials Results for Spacecraft Application Proceedings, NASA CP 3257, October 1992, page 21.
- 21) Proceedings of the Solar Maximum Repair Mission Study Workshop, NASA GSFC Report 408-SMRM-79-0001, May 1985.

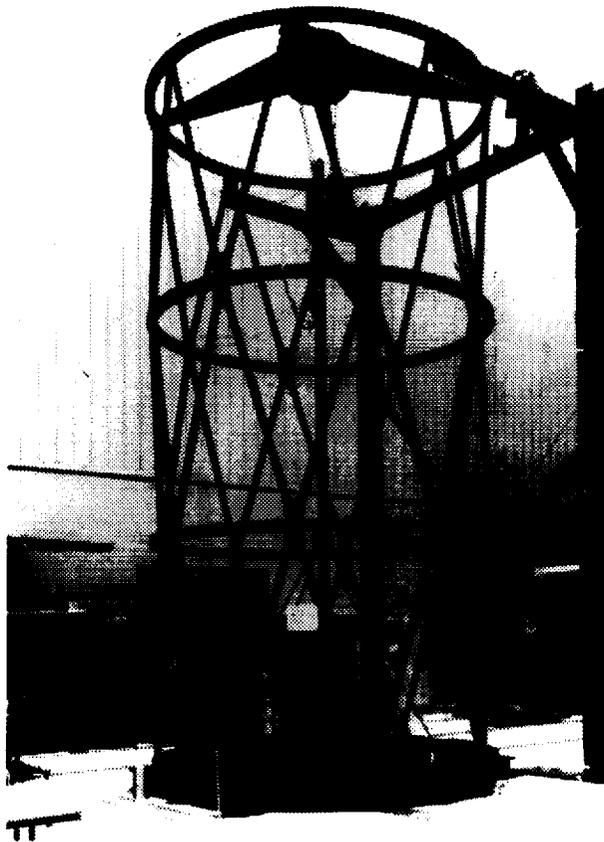


Figure 1. Hubble Space Telescope Optical Truss Assembly

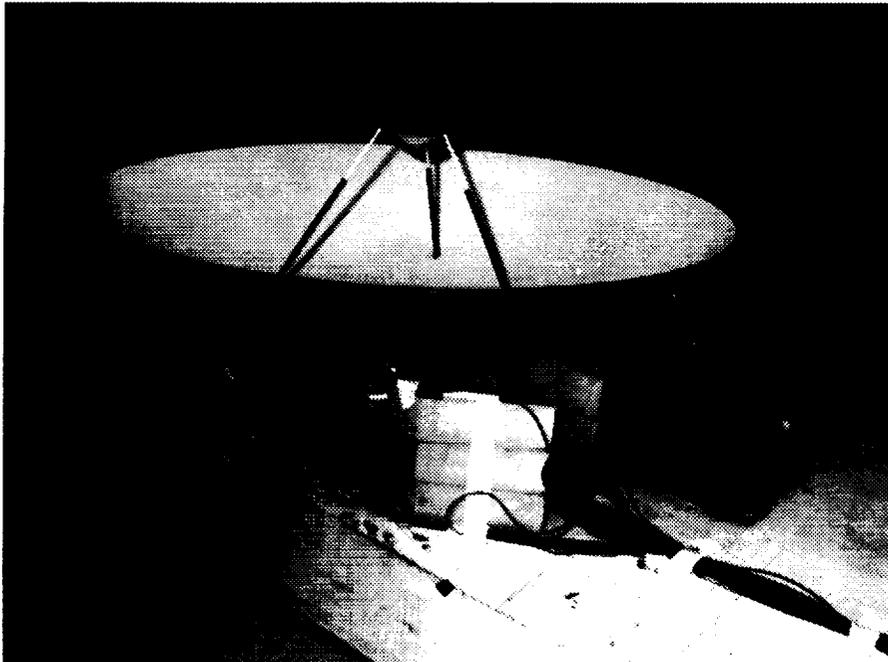


Figure 2. 6 Ft. Diameter Graphite/Epoxy Antenna

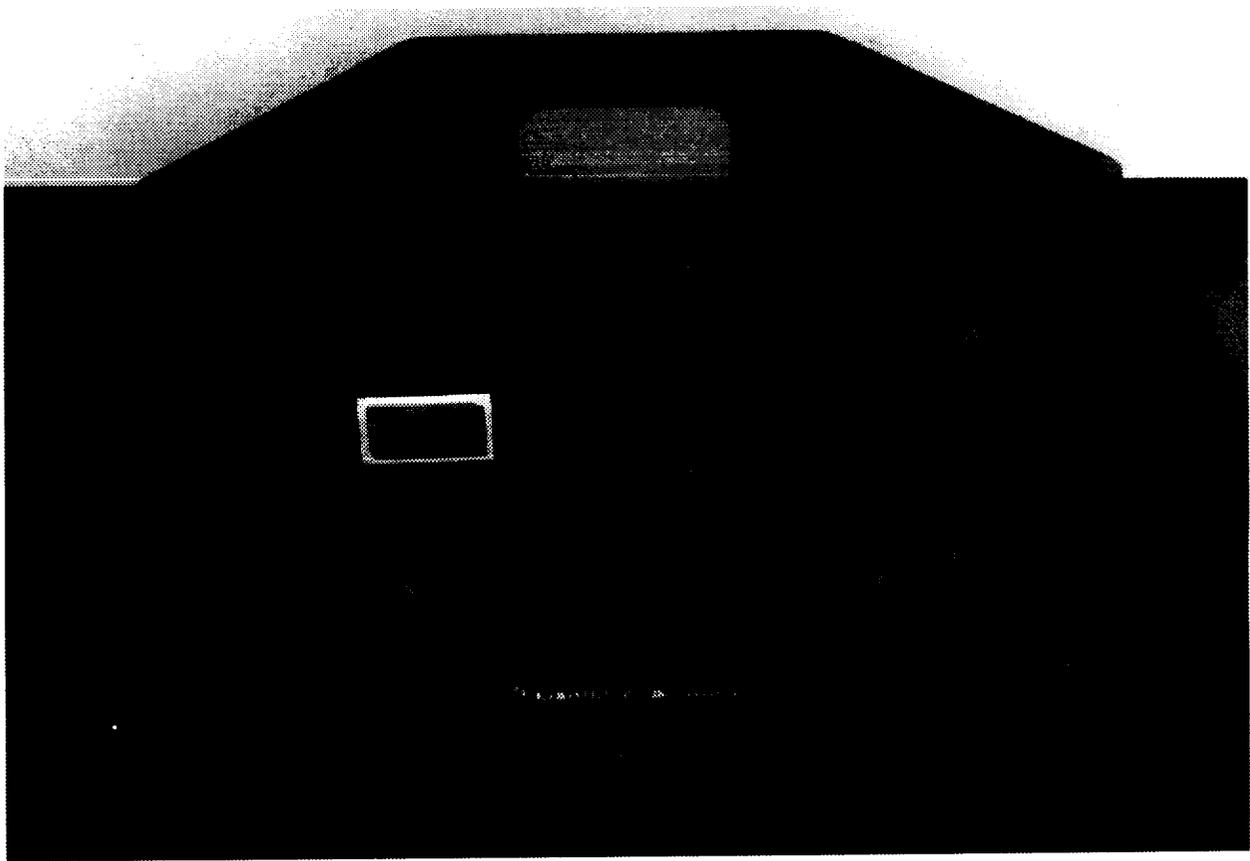


Figure 3. Prototype Composite Spacecraft Bus Structure

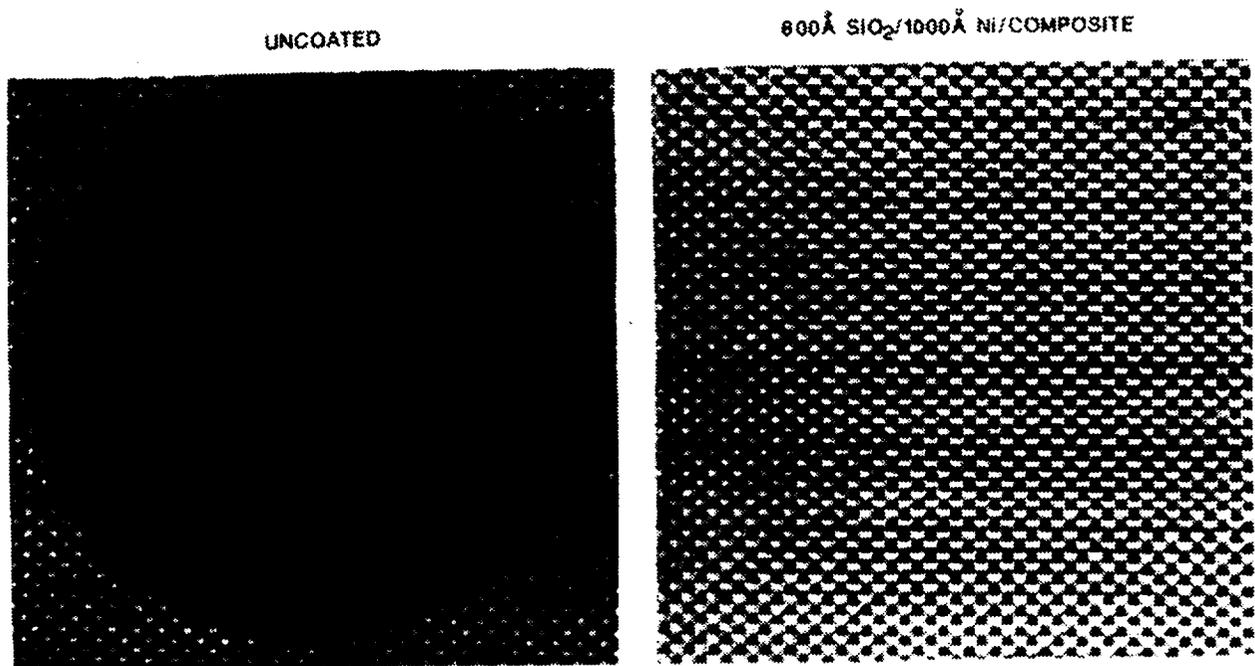


Figure 4. Bare And Protected Graphite/Epoxy Specimens Flown On LDEF's Leading Edge (Photo Courtesy of NASA LaRC)

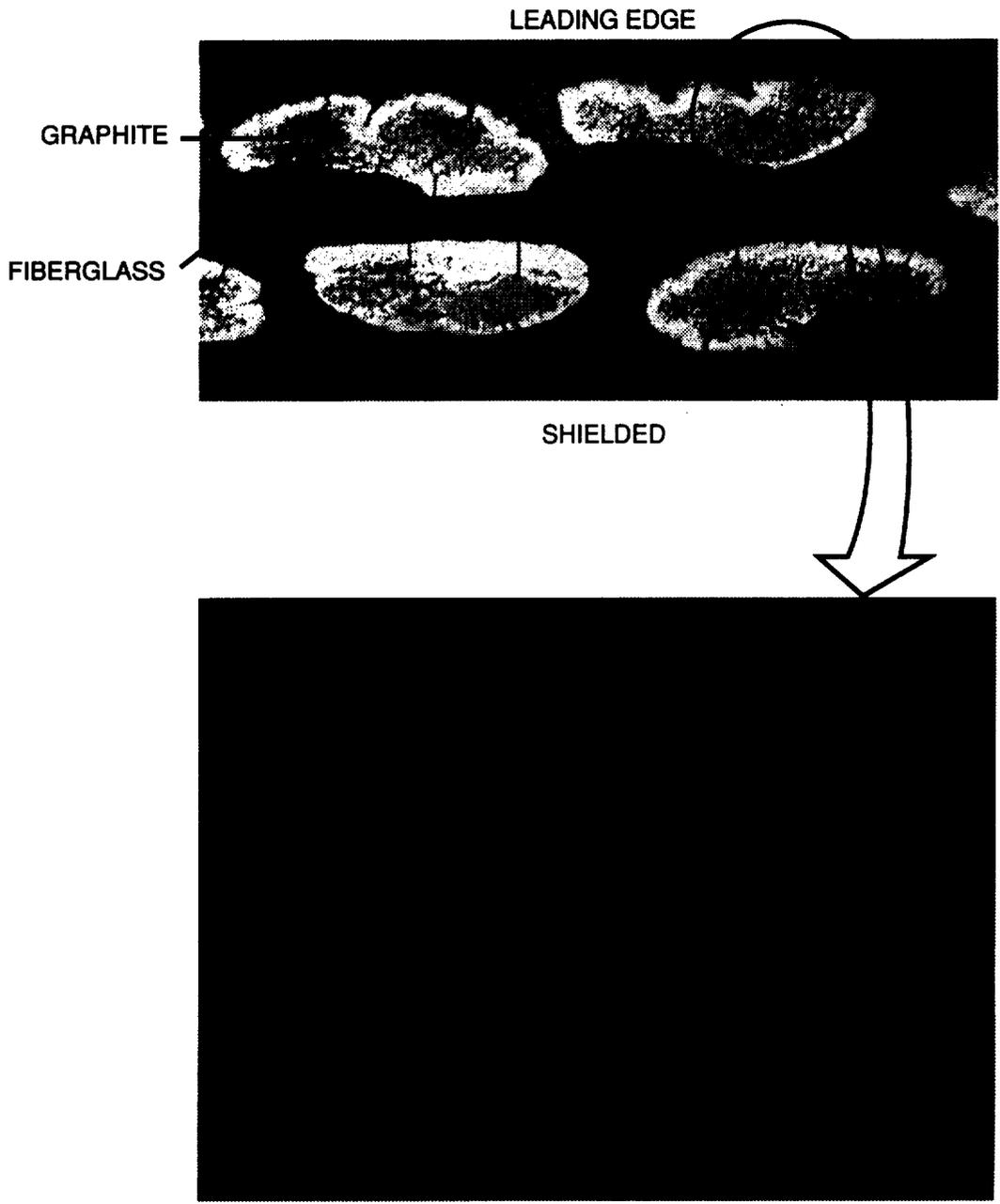


Figure 5. A-276 Coated Graphite-Fiberglass/Polysulfone Composite

OPTICAL PROPERTIES (a/e)

LEADING EDGE
(0.19/0.00)

CONTROL
(0.14/0.90)

TRAILING EDGE
(0.34/0.89)

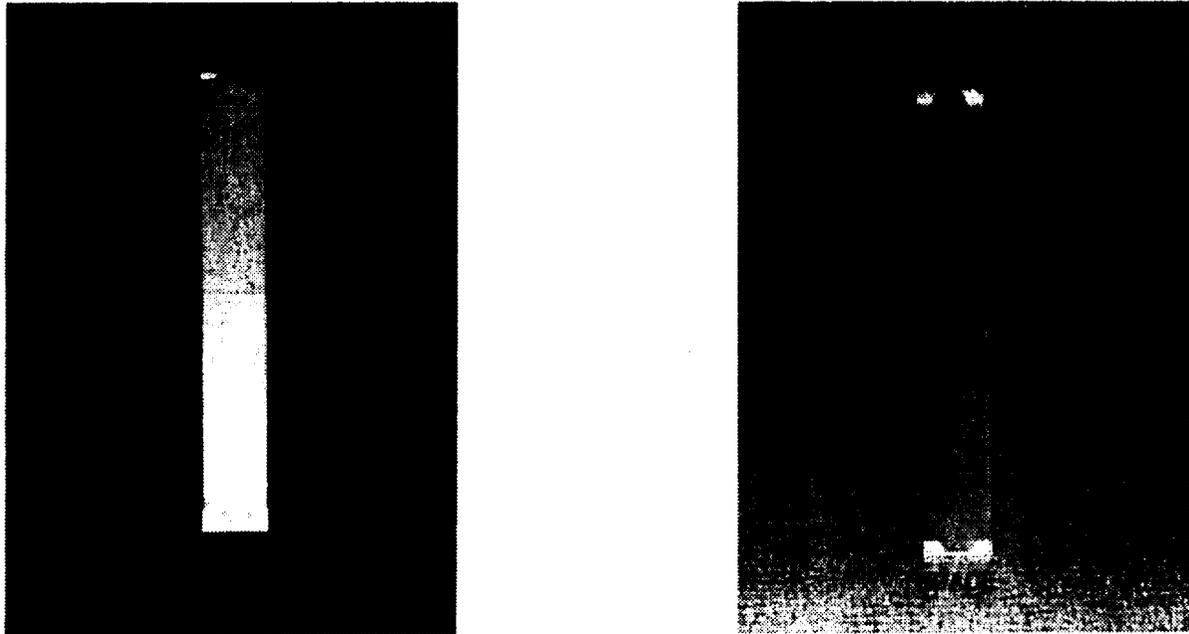


Figure 6. Effects Of LDEF Exposure On S-13G (Photos Courtesy of The Aerospace Corporation)

OPTICAL PROPERTIES (a/e)

LEADING EDGE
(0.60/0.73)

FACING INTERIOR
(0.66/0.78)

TRAILING EDGE
(0.75/0.78)



Figure 7. Effects Of LDEF Exposure On Leading Aluminum (Photo Courtesy of The Aerospace Corporation)

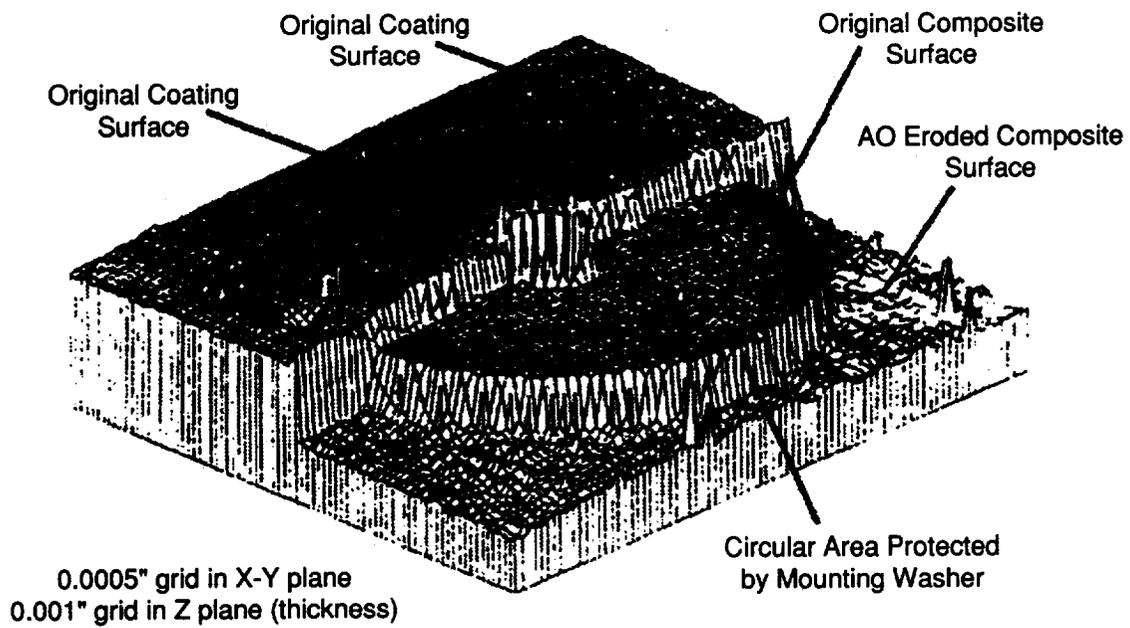


Figure 8. Three-dimensional Plot of Profilometry Measurements Taken From A Partially Coated Graphite/Epoxy Panel

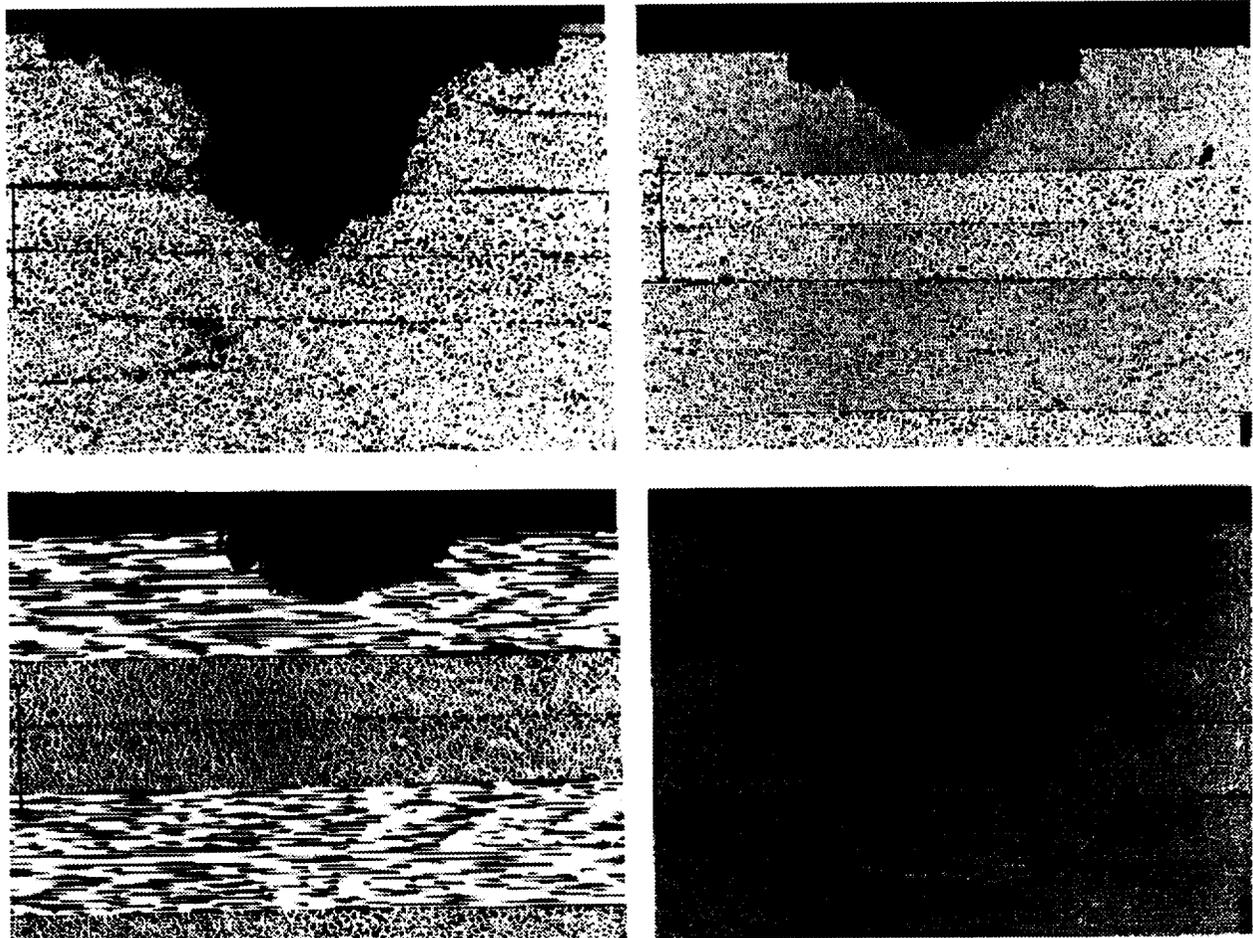


Figure 9. Impact Craters In Graphite/Epoxy